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EDITED BY EDWARD HART, Ph.D.,

PROFESSOR OF ANALYTICAL CHEMISTRY, LAFAYETTE COLLEGE.

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I. SOME EXPERIMENTS ON AMERICAN OIL OF TURPENTINE.

BY J. H. LONG.

As is well known, different kinds of turpentine oil differ from each other in marked degree in their action on polarized light. While the French oil is laevo-rotatory, the American and Russian oils are dextro-rotatory. The degree of rotation is not constant, and the greatest variations seem to be found in the American oil. The explanations offered for these differences have not been wholly satisfactory, and a few years ago I began the collection of specimens for examination, with the hope of throwing further light on the subject.

While the polariscopic tests have not shown all that I looked for, they have given some definite results of value, and will be explained at length later. In collecting samples for study, the question of purity frequently presented itself, and I found it necessary to look over the various tests proposed. In this way several practical points were brought out, which I believe worth putting on record. I will also add several details regarding the production of turpentine, as some of the statements in the text-books are misleading on this point. For much of this information I am indebted to Mr. E. B. Martin, of Louisville, Ky., who is probably the best American authority on the practical parts of the subject.

THE DISTILLATION OF TURPENTINE.

By far the largest proportion of our American turpentine is obtained from what is known as the "long leaf" yellow pine (*Pinus Australis*). In certain localities the "loblolly" or "old-field" pine (*P. taeda*) is abundant, but the oil obtained from it is but a small part of the whole. The same may be said of the "pitch" pine (*P. rigida*) and the "swamp" pine or Cuban pine (*P. Cubensis*).

This Cuban pine, called also "slash pine," is said to produce a good yield and high grade of turpentine, but the trees are not abundant. For the purpose of collecting the crude turpentine or "gum," pockets or "boxes," capable of holding about one half gallon, are cut in the tree a few feet from the ground. A large tree may have three or four of these boxes. They are cut during the winter months, and in the spring and early summer the exudation oleo resin collects in them. As often as necessary the contents of the boxes are dipped out and taken to the stills in barrels. To facilitate the collection of the "gum" in the boxes grooves or "streaks" are cut in the tree above each box. The exudation collects in these streaks, and gradually flows down into the boxes. The boxes cut in new trees are called "virgin" boxes, and the "gum" found in them, which is white and of the consistency of honey, is called "virgin dip." The "gum" collected in the boxes in the following years is called second year dip, third year dip, and so on. As the gum flows down the streaks to the boxes a part of it, in contact with the air and sun, becomes hard and adheres to the tree. In the autumn this is removed by a hatchet or tomahawk with a long handle, and is called first year scrape, second year scrape, third year scrape, and so on. After the exudation of the gum has ceased, the pots are taken from the trees and the trees are chipped. In some localities the practice of cutting boxes and gathering gum is kept up for several years, and the trees are finally chipped. The dip from the virgin boxes is of a higher grade than that of the later years.

[illegible] is carried on in [illegible] the gum. The stills [illegible] At one time it was [illegible] was added so that [illegible] The turpentine [illegible] as [illegible] the [illegible] It is usually sent out from

merce without further purification, although it holds a slight amount of water in solution.

A barrel of "gum," as taken to the still, weighs about 280 pounds (127 kilos), and yields from 7 to 9 gallons (26.5 to 34.1 liters) of the oil. The weight of rosin left in the still is about four times as great as that of the oil obtained.

The American production of turpentine is about 300,000 barrels per annum, of which over one-half is exported, chiefly from Savannah and Wilmington. Small shipments are made from Charleston, New Orleans and Mobile.

ADULTERATION OF TURPENTINE.

Turpentine, as sold in quantity, is not largely adulterated at the present time, although the reverse is generally supposed to be the case. That sophistication is not more commonly practiced, is mainly due to the watchfulness of a few large dealers, who expose a fraud as soon as discovered. Among the liquids which have been mixed with oil of turpentine, in the way of adulteration, the light petroleum products hold the first place. These may be added to the still with the "gum," as is done in the case of a certain "patent" oil made in small amount in several places, or they may be added to the oil in the tanks or barrels. A petty form of adulteration is sometimes practiced in this manner: A few gallons of oil are withdrawn from a barrel through the bunghole, and the loss is made up by adding benzine. The result is known as a "bunghole mixture."

Another adulterant, but one rarely met with in this country, is rosin spirit, a light volatile liquid formed in the dry distillation of rosin. It is not produced in the United States in quantity sufficient to give it importance as an adulterant. Cotton-seed oil has also been suggested as an adulterant, but if used at all, it must be in the manufacture of cheap paints and varnishes. While adulteration on the large scale is rare, it appears to be more common in the product sold by small retail dealers. The various sophistications can be detected by the following tests, which I have confirmed by recent experiments.

1. *Specific Gravity.*—The specific gravity of pure American turpentine varies within narrow limits, according to Allen (*Com. Org. Anal.* **2**, 437), between .864 and .870. My own tests

on thirteen samples distilled from fresh gum in the laboratory showed results varying between .8622 and .8655, water at 15 degrees being taken as unity. With pure commercial samples, I found the density to vary in a large number of cases between .8656 and .8748. The results here run higher, probably because of the presence of oxidation products due to atmospheric action.

The petroleum products which could be used in practice for the sophistication of turpentine have all a density much lower than this, as shown by the following table containing results of tests of standard American grades. The specific gravities were taken at a temperature of 15 degrees C., and refer to water at same temperature as unity.

Gasoline,	88	degrees	B.	sp. gr.	.6508
"	74	"	"	"	.7001
Benzine,	63	"	"	"	.7306
"Standard White,"	110	"	fire test	"	.7999
"Water White,"	150	"	"	"	.7918
"Head Light,"	175	"	"	"	.7952
Mineral Seal				"	.8293
Paraffine Oil				"	.8906

A mixture of 95 volumes of a turpentine, having a density of .8680, with 5 volumes of each one of these oils, gave results as follows:

With 5 vols.	Gasoline,	88	degrees	B.,		sp. gr.	.8568
" "	"	74	"	"		"	.8595
" "	Benzine,	63	"	"		"	.8606
" "	"Standard White,"	110	"	fire test		"	.8637
" "	"Water White,"	150	"	"		"	.8632
" "	"Head Light,"	175	"	"		"	.8638
" "	Mineral Seal,					"	.8656
" "	Paraffine Oil,					"	.8688

With mixtures like the above, it is evident that 5 per cent. of gasoline 88 degrees, gasoline 74 degrees, and benzine 63 degrees, is clearly indicated by the specific gravity test. Using the same turpentine, an admixture of petroleum products similar to "Standard White," "Water White," and "Head Light," could be detected if present to the extent of 10 per cent.

With a heavy grade of turpentine, the detection would be doubtful. However, an adulteration as great as 20 per cent. would be indicated even with a turpentine having a density of .875.

For the detection of ordinary rosin spirit, the specific gravity determination is of little practical value, as some grades of the spirit have a density greater, while others have a density lower than that of turpentine. Rosin oil, however, is heavier than turpentine.

Fatty oils added to turpentine could readily be detected by this test because of their relatively high specific gravity.

2. *Boiling Point.*—In the examination of a large number of pure commercial samples of turpentine, it was observed that the boiling point was uniformly at 155 to 156 degrees, and that 85 per cent. of the sample distilled between 155 and 163 degrees. The distillation is practically complete below 185 degrees. From this it appears that a determination of the boiling point coupled with a fractional distillation may be of the highest value in detecting adulteration with petroleum products.

The initial and final boiling points of the eight mineral oils referred to above were as follows:

		Initial.	Final.
Gasoline,	88 degrees.	About 40 degrees.	About 110 degrees.
"	74 "	" 55 "	" 125 "
Benzine,	63 "	" 95 "	" 165 "
"Standard White,"	110 "	" 130 "	Above 360 "
"Water White,"	150 "	" 140 "	About 310 "
"Head Light,"	175 "	" 160 "	" 315 "
Mineral Seal,		" 230 "	Above 360 "
Paraffine Oil,		" 300 "	" 360 "

By the initial temperature here is meant not the point at which the first few drops passed over, but the temperature reached when about 1 cc. of 100 taken had passed over. The presence of 5 per cent. of mineral oils with turpentine would readily be shown by the tests, as was found by experiment.

3. *Flashing Point.*—Much importance is attached to the flashing point test. According to Redwood, the flashing point of average American turpentine is 33 degrees C., which is much lowered by the presence of small amounts of volatile petroleum products. In the apparatus which I employ for such tests, a form similar to that suggested by Stoddard (*Am. Chem. Jour.* **4**, 287), I find 32 degrees C. as the usual flashing point. Experiments were made on mixtures containing 95 volumes of turpentine with 5 volumes of several oils, with the following results:

With	Gasoline,	88	degrees,	flashing	point	below	15	degrees C.
"	"	74	"	"	"	"	19	"
"	Benzine,	63	"	"	"	about	22	"
"	"Standard White,"	110	"	"	"	"	32	"
"	"Water White,"	150	"	"	"	"	33	"
"	"Head Light,"	175	"	"	"	"	34	"
"	Mineral Seal,			"	"	"	35	"
"	Paraffine Oil,			"	"	"	36.5	"

These figures show that very small amounts of the lighter petroleum products have a marked effect, while 5 per cent. of the common burning oils would escape detection by this test.

4. *Vapor Density.*—The vapor density of turpentine being much higher than that of the light petroleum products sometimes used for adulteration, I thought it desirable to test the value of this determination, as an indication of purity. The Victor and Carl Meyer method by measurement of displaced air (*Berichte*, 1878, p. 2253) is very convenient for this purpose, and in my experiments was employed with ethyl benzoate as heating liquid. In the first tests a sample of fresh turpentine was distilled fractionally, and the portion distilling at 155.5 to 156.5 degrees was taken for experiment. Two trials gave a vapor density of 4.68 and 4.66, corresponding to molecular weights of 135.11 and 134.53. Another sample treated in the same way gave 135, as the molecular weight. Ordinary commercial turpentine not fractionated gives usually somewhat higher values, as shown by the following table. About 150 mgms. were taken for each trial.

No.	Vapor Density.	Molecular Weight.
1	5.05	145.8
2	4.73	136.6
3	4.89	141.2
4	4.86	140.4
5	4.88	140.9
6	5.11	147.7
7	4.92	142.1
8	4.87	140.8
9	4.98	143.8
10	4.88	140.9
11	4.80	138.6
12	5.08	146.7
13	5.05	145.8
14	4.89	141.2
15	4.80	138.6

It will be remembered that in the fractional distillation of 100 cc. of these turpentines, about 85 cc. is obtained between 155 and 163 degrees C., while in some cases the distillation is not completed below 180 to 185 degrees. In No. 13 the temperature of distillation reached 190 degrees. Both tests indicate the presence of compounds heavier than the pure terpene $C_{10}H_{16}$.

The light petroleum products known as 88 degree gasoline, 74 degree gasoline, and 63 degree benzine, consist essentially of hydrocarbons having a molecular weight below that of turpentine. The 63 degree benzine contains chiefly C_8H_{18} and C_9H_{20} (according to Schaedler and Allen). A commercial sample tested in the laboratory began to boil at about 80 degrees, and was completely volatile under 150 degrees. Most of it distilled between 105 and 130. A determination of the vapor density gave 4.09, corresponding to a molecular weight of 118.1. A second sample, distilling at a somewhat lower temperature, gave 3.81 as the vapor density, with 109.9 as the corresponding molecular weight. An experiment was made by mixing equal volumes of turpentine, No. 8, of the above table, and the benzine sample having a density of 4.09. A small amount was weighed out for the test, the result of which gave 4.42 as the vapor density, with 127.5 as the corresponding molecular weight. This is a little lower than one would expect. A small addition of benzine can be shown by proceeding as in the following experiments:

A sample of turpentine was fractionated, and the portion boiling at 156 degrees saved. This gave a density of 4.67. A mixture containing 97 cc. of this turpentine and 3 cc. of the benzine of the last experiment was made and distilled fractionally, the first 10 cc. being saved. This was used for a vapor density determination, which gave as the result 4.56, corresponding to 131.6 molecular weight. In another trial 90 cc. of the same turpentine, and 10 cc. of the benzine were mixed and distilled, 10 cc. being saved. 4.34 was found here as the vapor density corresponding to a mean molecular weight of 125.3.

By taking the first portion of the distillate, it is possible in such cases to show readily an admixture of light petroleum products, but the method naturally fails with heavier products. A certain

brand of commercial turpentine known among dealers as "patent" oil, and which contains a kerosene of moderately high test, was tried in the same manner. The vapor density of the whole product was found to be 5.49, corresponding to a molecular weight of 158.5, while the first portion of a distillate gave a density scarcely differing from that of turpentine. A low vapor density would be found in a distillate containing rosin spirit.

5. *Distillation with Steam.* I have made a number of tests in this manner, as recommended by Armstrong, and obtained results which fully confirm his. The method is valuable for the detection of vegetable oils or heavier petroleum products.

6. *Nitric Acid Oxidation.* Wm. Burton (*Am. Chem. Jour.* **12**, 1021) has shown that a fair quantitative measure of the petroleum products present in a turpentine may be made by treating the sample with fuming nitric acid in the cold. By slowly dropping 100 cc. of the turpentine into about [illegible] cc. of the fuming acid in a flask immersed in cold water, the turpentine is gradually oxidized to acid compounds soluble in hot water, while the petroleum is left practically unattacked. At the end of the reaction it is simply necessary to wash the product several times with hot water to dissolve the oxidation compounds, separate with a funnel, and measure the paraffine residue. This is probably the best quantitative method yet proposed, and in my hands has given fairly good results.

7. *Other Tests.* Numerous other tests have been given for the detection of adulteration in turpentine. Some of them are valuable, but many are useless and often misleading. As an illustration, I will describe one which is published in the widely circulated *Paint Oil and Drug Review* of Dec. 27, 1892, as "An Absolute Test for Turpentine," and which has been made known to dealers and producers by means of a printed circular.

The test is carried out by adding a few crystals of potassium nitrate to the turpentine and warming gently. If the crystals remain white the oil is said to be genuine, but if they turn brown it is said to be adulterated. This is supposed to indicate adulteration with petroleum products, but how it does so is not explained. Several experiments I tried gave very different results.

The following is probably an explanation of what takes place, and will show the fallacy of the test. With perfectly pure potassium iodide, fresh turpentine which has not been exposed to the air gives practically no coloration, while with older samples I have observed a marked color, which is undoubtedly due to the action of hydrogen peroxide formed in the turpentine by contact with air. This can be readily shown by experiment. If a fresh turpentine which does not react with the iodide is exposed freely to the air for some days, or even shaken in a partly filled bottle a short time, a reaction will appear in a few seconds after adding the crystals. Kingzett (*Jour. Soc. Chem. Ind.* 1886, p. 7) has called attention to the large amount of hydrogen peroxide formed by the oxidation of Russian turpentine. The yield from American turpentine is less, but still important.

Iodide of potassium containing iodate would give a reaction with samples of turpentine containing petroleum products from which the sulphuric acid of the refining operation had not been thoroughly removed. Experiments made with pure iodide, fresh turpentine and acid free petroleum gave no reaction whatever. The test is therefore without value.

A study of the optical properties of turpentine I reserve for a communication to follow.

CHICAGO, Dec. 28, 1891.

PYRITES AS A MATERIAL FOR THE MANUFACTURE OF SULPHURIC ACID.

BY WM. H. ADAMS, M.E.

[*Continued from Vol. V, page 670.*]

It will now be in order to take up the descriptions of mines in our own country, beginning on the northern boundary.

Newfoundland is generously supplied with true pyrites ores, both the iron and the copper sulphides being found in abundance, with well marked and economically placed deposits of the best character, which, however, must always be handicapped by the necessity for mining and shipping the major part of the stocks during a short summer season. These ores have been well received by con-

sumers in the United States, as they contain on the average about 48 per cent. of sulphur; are free burning, and the cinders from the lump ores are readily saleable to iron furnaces in the neighborhood.

The mining and shipping must always operate to the disadvantage of these ores, and were it not for the iron contents, there could be no profit in handling them, even with duties removed, as of late.

What the future may have in store for these great supplies of commercially valuable products must be a question entirely in the hands of centrally located mines in Europe and America, which, with copper contents, are better able to control the markets of the United States, their by products being even more valuable than from the Newfoundland ores.

In Quebec district, Canada, the entire supply of ores, averaging about 34 per cent. sulphur, is taken over by the owners, and really makes no impression on the trade of the country other than known for the past ten years. The limit of production in the case of the Capelton deposits was reached sometime since, and with depth below the 1500 foot levels, the supply must decline gradually. It is interesting to note in connection with the growth of the trade in acids from these ores that they were first utilized for this purpose by General Adams, who operated the mines from 1864 to 1878. He erected the first chambers to work the copper ores, in the year 1868 (?), and may fairly be considered the pioneer in the industry, inasmuch as no other chambers were used continuously for utilizing ores for many years after that date. These mines have supplied to the trade of the country at least [illegible] tons of commercial acids up to date, all of which would have been wasted if the ordinary processes of copper workings had been carried on, i. e. wasting the sulphur by the initial roasting.

This represents a saving to this country of at least $1,[illegible], which would have been paid to foreign countries for the amount of sulphur thus replaced by ores.

The Milan mine in New Hampshire, on the line of the Grand Trunk Railway [illegible] miles from Portland, Me., was opened in a practical manner in the year 1881. The ores of this district resemble some of the Spanish mine ores, and are said to be in the

same geological formation. Several lenticular deposits have been opened, with an average width of 8 feet, and maximum width of 40 feet (*vide, Mineral Resources of the U. S.*, 1887).

Many features of great interest to students will be found along this belt—several miles in length,—although workings have been carried on at but one location. It is said that the foot wall of argillaceous slates is at all times well defined, but that nothing like a true hanging wall was discernable for many years, and cannot be said to be well defined even now.

Considerable copper ore is found in bands, or beds, and occasionally pockets of galena (containing over 100 ounces of silver per ton) are found closely associated with the copper; also zinc blende in bands of unequal length and depth. The method of working this deposit was by open cut, 200 feet long, and the full width of the paying ores. For some reason, the output has been limited for so promising a development, a very small tonnage having been sold, and that only in the immediate section of country tributary to the mine—Boston, Portland, etc. Copper was smelted from the portion of the ores for a time, but as the sulphur contents are said to be never less than 40 per cent., it would seem as if the methods adopted by other mines of similar character would result in greater profits, and it must eventually be the case that all the ores from this section will become sufficiently valuable to be worked in one of the larger cities, and worked for all the contained metals. Average cost of mining, sorting, and all cost of management, is stated to be about $2 per ton of ore shipped, and at these figures there must surely be a large profit, unless there be some unknown cause for lessened values in products.

To the southwest, on the same belt of pyritiferous-bearing rocks, are located the Vershire group of mines, at West Fairlee, Vt. The Ely, Union and Corinth are best known, and a little distance away is the Elizabeth mine, near South Stafford, Vt.

The former mines have been fully described many times, and by expert engineers, during the past forty years, as occupying the usual position in talcose schists near the granites, with a dip of about 26 degrees from the horizontal, and all the ores so far disclosed being in contracted lenses, say 200 feet greatest length, and 6 to 15 feet wide—greatest depth 1800 feet.

Copper having been the only value, the sulphur contents being below 35 per cent., these mines are mentioned here as examples of large mining and smelting, extending over a long period of time, and as having favorable features for study, although no work of consequence is at present being done on the belt.

The Elizabeth mine, however, almost unknown in literature, has developments which rank with the larger mines further south. We find here the usual lenses, principally of pyrrhotite, and comparable to those of Carroll County, Va., Ore Knob, N. C., and Ducktown, Tenn., which in a similar manner are impregnated with chalcopyrite in sufficient quantities to invite and inaugurate quite an extensive industry in mining and smelting for copper. The ore body as disclosed is about 200 feet long and 25 to 65 feet wide. No great depth has been gained as yet, the surface ores being in sufficient quantity to satisfy workings for years to come.

This deposit is mentioned for its many interesting geological features. None of the ores are suitable for acid making, but much of it is claimed to be exactly suitable for "Bessemerizing" and with the additional knowledge we are gaining year by year, there may yet be a grand future for this mine, known since 1776 as the great copperas (iron proto-sulphate) producer.

In Rowe County, Mass., the Davis mine has been opened and favorably known to the trade since the year 1881. This body of ores belongs to the family of true pyrites (iron bi-sulphide) and promises for many years to be well known as a producer. Developments are made for 600 feet in length, 60 feet in depth, and from 7 to 25 feet wide; the foot wall of mica schists and the hanging wall of chloritic slates.

According to Government reports, the cost of mining is $1.00; teaming to railway station, $1.00; and railway freights to New York or Boston, $2.00. Analyses has already been given in the table.

The Anthony's Nose deposit of pyrrhotite has been abandoned for many years past, and I never was worthy of being opened for sulphur or copper contents of the ores. Further down the belt are found the magnetites of New Jersey, and the pyritiferous slates of Maryland, both belonging to the main belt of the Atlantic

ghanies, but not necessary to be elaborated as deposits emphasizing our subject.

We next come to the Louisa County, Va., deposits, geologically almost identical with those at Milan and Davis mines, with contact rocks, quartzose and gneissic, as in Spain. Staurolites and garnets are found commonly in the schists, some of the garnet matrixes being found as slabs several feet square, studded with the crystals, from pin-head size to that of large walnuts.

My intimate connection with these mines since they were opened in the year 1883 has deepened the impression as to origin of the mineral matter deposited all along this Eastern belt. In the light of every fact disclosed by workings to a depth of 500 feet, and of examinations of other deposits, I cannot doubt that they are bedded veins, their origin being contemporaneous with the surrounding stratas of varying constituents.

The Louisa County deposits are about five miles in length from north to south, and occupy a series of headlands or apexes at the extreme west side of the main dividing ridge of mineral bearing schists, so prominently disclosed at this particular locality.

All of the known deposits have been exploited during the past fifty years in extraction of the overlying iron ores (limonite), and the underlying masses of pyrites seem to be directly proportioned to existing surface excavations. Thus we have several localities where the iron pits have been opened to a width of 60 feet between walls, and the workings for pyrites below the iron hat for 200 feet or more has shown the same relative width.*

Iron pits are commonly met with from the line of the Chesapeake & Ohio Railway to the Rappahannock river, and it has always been a subject of argument among explorers as to reasons for the existence of limonite over all this section, underlaid, however, with pyrite only in this and one other section of the State. The schists appear to be the same as found elsewhere. The associated minerals, with their matrixes, admit of no very different classification, yet the fact remains that here we find vast beds of iron ores contaminated somewhat with undecomposed pyrite to a depth of 50 to 60 feet, and immediately below this iron ore the

*See "The first Iron Blast-furnaces in America." Trans. Am. Inst. Min. Eng., 1891.

solid unaltered pyrite is found in extent comparable only to the deposits of Norway, Spain and Portugal.

Almost side by side we find the pyrites and the gold deposits, which are contemporaneous with the slates themselves, the gold in these slate beds evidently being derived from the destruction of the older rocks. Prof. Emmons (writing in 1856) says all this gold belongs to the paleozoic period, and came in the shape of sediments. Prof. Kerr says subsequently to its deposition it has been acted upon by chemical agencies, dissolved and precipitated again, sometimes assuming a crystalline structure, sometimes accumulates in strings; forms lenticular and more highly auriferous masses in the beds, and is associated with crystalline quartz, pyrite, chalcopyrite, galenite (blende, mispickel, etc. All of these characteristics are met with along this central divide, in the streams parallel to same, and in the breaks and water courses leading to the creeks. At the Walton gold mine some of the richest examples ever shown of gold in galenite associated with mispickel were taken out within 100 feet of the surface.

It is a most interesting study to trace the mineral bearing belt which here finds so promising conditions for the segregation of enormous amounts of minerals and of so many kinds.

To the northward the greatest lines of force were evidently exerted by a sudden depression of primitive rocks (which now lie under water off the east shores of Virginia and Maryland, in a direct course from Newfoundland to the middle Carolinas.

We have nowhere along our own mineral belt from Vermont to Georgia such gigantic dykes, faults and dislocations as are plainly observable in the localities named, and the depression of a mountain chain equivalent to our Alleghanies can alone account for the mighty breaks across the stratification which gave place to the Delaware and Chesapeake bays, the Potomac, James and minor waterways.

Admitting the presence at one time of this east mineral range and all the problems which meet us along our very narrow belt are easy of solution. The existence of the quartzose lentils from the Potomac to the James rivers, the [illegible] of the western slopes of the same belt, the mineralized zones in limestone at the

base of the Blue Ridge; the copper in various forms and at irregular distances in Maryland and Virginia—all these problems, so puzzling, are answerable when the source is admitted to be from an eastern chain of mountains lost to sight by some great cataclasm of nature.

On the eastern side of the pyrites belt the chists are granite, micaceous and argillaceous, with workable beds of mica, kaolin, graphitic talc, etc., etc.

On the westward side heavier bands of granitic schists come to surface with silicious clays, firestone, soapstone, flints, etc., etc.

At the northern end of the outburst of pyrites, the chloritic, steatite and talcose slates are cut squarely across by some agency and form a dam, over which the Contrary creek flows on its way to become a part of the North Anna river. The North Anna in turn cuts the stratification at a point about 7 miles further north, and these two cross-breaks give us the data for geological research in both directions. Where the Contrary creek crosses the pyrites belt, there are radiating breaks in the surface like spokes in an immense wheel—the position of the hub acting as a basin or an eddy for the accumulation of sedementry matter for ages past.

Within the distance of a-half mile over half a million dollars in stream gold has been taken out since 1820, and for several miles up and down the creek large amounts of gold have been found.

I mention these features to show how exactly similar the deposits of this section are when compared to Canada, Vermont, Massachusetts and other points along the belt, and how closely the several minerals are associated, yet how exceedingly difficult it is to find, throughout Virginia, any real source for the vast amounts of mineral. In Canada, to the eastward and westward of the Capelton mines, there are millions of tons of diluvium distinctly foreign to the locality with glacial detritus apparent.

South of the Potomac we have no evidences of glacial action, no detritus other than from the primitive rocks themselves, and every evidence of the deposition of minerals from solutions, chemical actions which dissolve and precipitate year after year, in a never-ending cycle.

The first property from the northern end of the outburst of pyrite is owned by the Sulphur Mines Co., of Virginia, and comprises

about one mile length on the beds. The extreme northern limit of the headlands produce the cleanest and best grade pyrites, the middle, fin-shaped, out-break is pyrrhotite and the southern break is zinciferous pyrite, with lead and possibly silver as depth is gained.

Only the first named deposit is being worked at present.

The second property is owned by Philadelphia parties, but as only exploratory work has been done so far in the rise of ground at the southern end of the lands, there is no data to form opinions as to character and values of the ores.

The third property is owned by the Arminius Copper Mines Co. with about three quarters of a mile length on the beds, a mineralized belt from end to end. In the bed of a small water-course the lowest depression on the lands of this company, there is disclosed the outcrop of a considerable deposit which was opened [illegible] years ago for copper and thus gave the name to this property. Reopened of late years there has been found a very peculiar pyrite deposit, with sulphur contents about [illegible] per cent, with magnetic iron in finely divided grains, with chalcopyrite containing silver and gold to amount to six $ [illegible] per ton and a most distinctive matrix of graphitic slate. At no other locality on the belt except at Tallapoosa, Ga., have I seen anything to resemble this ore and its accompanying gangue.

To the south-west the ground rises [illegible] feet to the location of the men working shafts of the company [illegible] feet distant, and here we find the deposit [illegible] feet length [illegible] feet depth and average width [illegible] feet. The pyrites mined from this deposit and shipped at the [illegible] are [illegible] so well known to need special comment at [illegible] having already been given in the table of [illegible]

The [illegible] property [illegible] the course of the [illegible] The presence of an [illegible] between the last named property [illegible] West [illegible] name [illegible] visit [illegible]

The fifth property of the group [illegible] south of the

Chesapeake & Ohio Railway, but has no development worthy of mention.

Both the first and third named mine properties are connected with the main line of the Chesapeake & Ohio Railway by standard gauge branch railways, constructed and owned by themselves. They are thus in direct communication, with all the large cities of the Western, Middle and Southern States, as well as within easy shipping distance of Richmond, Va., 60 miles; also but 150 miles from Newport News and Norfork, Va., where vessels at all times are obtainable for transport of the pyrites or their products to any coast city of this country or abroad.

A peculiar advantage is secured by shipping at these ports, inasmuch as one-third the cotton crop of the South is marketed from Norfolk, and, as ballast in cotton ships, the freights to European ports is never over one dollar per ton, generally less.

I have already stated that shipments from the Louisa County deposits for the year 1891 will amount to at least 70,000 tons.

This replaces foreign brimstone to the amount of 30,000 tons, or an annual saving of over $750,000 in cash, formerly paid to owners of old world mines.

In this connection it should be understood that although this almost barren waste of mineral land has been known for the past fifty years, and has produced only small amounts of iron ores—worked in an exceedingly crude manner without appreciable benefit to the surrounding country, yet since the opening of the Arminius mines by the present owners, and their introduction into very general use of the granular ores which this district furnishes in greater quantities, there has sprung up a settled, orderly, prosperous community of nearly one thousand souls directly dependent upon the mines for their support, and this number is constantly being increased as the demand for ore increases. With supplies of ore now in sight, with added investments for the further treatment of these mine products, there will gather about this section many industries which employ labor and build up thriving centers of trade.

During the nine years of development work in Louisa County, Va., the sulphur from those ores has been sold for less than half the price of brimstone.

Do we realize the influence of such radical lessening of prices, made possible by utilization of home products of the soil?

The consumption of acid phosphate this year, in the Southern States alone, will exceed 600,000 tons, and the prices this year will be $4,000,000 less than paid for an equal quantity four years ago.

Were the pyrites of the Southern States fully utilized $1,000,000 would be saved to the South on the above tonnage.

Southwesterly from the Louisa county deposits there is but one development on the mineral belt near the James river, and that is in Buckingham county, where a small outcrop of copper bearing pyrites has been uncovered during the general search for gold. The developments now going on by a new company will practically test the deposit for quantity and value.

Floyd, Carroll and Grayson counties are well known mineral producers, and are often quoted as containing enormous bodies of low grade copper ores in pyrite. While the ores are commonly classed as pyrites, it is unfortunately the fact that few localities only have disclosed bulk sulphides of iron, the bulk of the ores being pyrrhotite, the same as already mentioned as found in large quantities at the Elizabeth mine in Vermont. Chalcosite and chalcopyrite is found in greater or less amount in these pyrrhotites, and over a long stretch of country. It is within the possibilities therefore that in the near future there will be introduced such economical methods of working this class of ores as to warrant the establishment of industries on a grand scale. All of the ore is silver bearing, and probably carries some gold, is remarkably free from arsenic, phosphorus, antimony, etc., so that admitting the absence of sulphur in paying quantities there are yet other products which would be commercially valuable when worked under one system.

By reference to a map of Virginia it will be seen that at present this mineral range from Floyd county, the northern boundary, to Ashe county, North Carolina, the southern end, is without direct railway communication. Were lines extended into this section the distance from existing markets and the excessive freight rates

in such mountainous regions would more than likely overcome the advantages which should accrue to so extensive deposits.

There is, however, no necessity for marketing these ores in the more northerly states, in opposition, perhaps, to other mines, as markets of equal importance, if not of greater extent, will shortly be opened within easy reach by rail, and the Southern States should properly draw their supplies from such sources as are found along their own mineral belts.

The Ore Knob mines, perhaps more favorably known than any other mine location of this Eastern belt, belongs to this group of deposits, and are but ten miles south of the Virginia state line.

The range lies 4,590 feet above sea level, as compared to 500 feet in Louisa county, yet the outcrop is the same gossan, or iron hat, and of the same mineral thickness. In shafting for the ores, no dead work has to be done except to pass through this iron gossan, never more than fifty feet, and the walls being almost vertical the mining of the beds, which are from ten to fifteen feet thick, is attended with little expense in timbering, etc.

Mining operations have been conducted along this belt since 1857, and it is but lately that copper works of the most complete character were in going shape, and successful, until the price of ingot dropped below the twelve-cent line.

These workings, carried on for many years, demonstrated to a certainty that ores of this class, containing less than three per cent. of copper, cannot be handled to a profit with ingot at twelve cents.

Location may be said to mean everything in the way of success or failure, and it is true that transportation problems were among the main causes for failure in this particular case. Such drawbacks are, however, a direct stimulus for improving every detail of working, so that costs in every department are lessened to meet the heavy charges for transport to market. The great improvements in roasting, smelting and refining of copper, gold and silver have come from this necessity.

With the settlement of the transportation problems and the erection of metallurgical plants to treat all the contained metals in these ores there promises to be a grand future for this district.

About 100 miles to the eastward are found the mines of the great gold belt, which extends from the Virginia line to Georgia.

This belt is from 5 to 20 miles wide and contains such well-known examples of large ore deposits as the Hoover, Gold Hill, Russell, Brewer and Haile mines, beside many others of lesser magnitude. They are too well known from frequent mention in geological reports, private descriptions, and every-day knowledge of their special characteristics to need elaborate mention here. But the entire belt will be the scene of renewed activity at no very distant period, when the values in sulphur, iron and precious metals are properly appreciated.

In a strictly mineral sense I class this belt of mineralized slates as among the grand natural wonders of this country, and no one can travel its length and breadth without marveling at the wealth in low grade ores, easy of access, enormous in amount.

That so much of anticipation and so little of realization has been the history of this section thus far is owing not to the lack of tonnage nor to varying values, but it may be said that causes which have brought disaster to enterprises along this mineral range are the same causes which have produced a like result in every prominent mining section of the world. Starting with the broad proposition that a close business management is as essential in mining as in every other enterprise and that there is a certain definite percentage of success and failure in all business, it can be proved, by examples exactly fitted to the conditions existing along this belt, that ton for ton and working up all the products, there will be found a greater average profit than in western ores.

I shall attempt to make this statement perfectly clear in every way further on basing my arguments on premises never yet brought forward with reference to these ores.

The Carroll and Ashe county deposits continue in a direct line into Georgia with Dahlonega as a center, thence to Alabama entering through Clebarne county where the well known Stone Hill mines were opened many years ago.

The upturned mineral bearing slates form a continuous divide from Maryland to the Coosa river in Alabama where they are entirely cut out and disappear. The waters generally flow to the north and south of this divide, that is to the Ohio and Mississippi rivers in the one direction and to the Atlantic ocean in the other.

Every creek, stream and gash along this divide is gold bearing

to some extent, the eastern slope furnishing mostly free gold and the western slopes oftener showing pyrites at or near the surface.

The free gold developments are not necessary to mention in this article. The pyrites, however, have received too little attention during all these years of prosperity to the South, and, so far as disclosed by the limited prospecting, have been so favorable a material for the manufacture of sulphuric acid that it is to be hoped a more liberal policy will be advanced and adopted from this time on which will bring them into the prominence they deserve.

The deposits near Dallas, in Paulding county, and the Tallapoosa mines in Harralson county, have already been mentioned by me.

They are mineralized zones of pyrite, with variable amounts of copper, iron, gold and silver found in the usual schistose slates, with a gangue which is easily separated by the commonest methods of mechanical concentration. Their mining, classification, treatment for extraction of the sulphur in acid manufacture and subsequent recovery of the contained metals, is one of the problems successfully worked out in the North on like ores during the past fifteen years, and now carried on in a large way near New York—250 tons daily.

The Stone Hill mines, in Alabama, consist of two large deposits of pyrrhotite; one of them proved twelve hundred feet in length.

The ores are intercalated in a micaceous schist of the Laurentian age, the surface altered into limonite by atmospheric agencies, and in the zone below the iron hat black oxide of copper has been found in large quantities, or more properly, a rich black sulphide containing about 30 per cent. copper.

The bed is a mixed slate and pyrites over 15 feet, and pyrrhotites for 15 to 20 feet greater width, the bulk of the ores from end to end carrying over 3 per cent. of copper, and except for the usual difficulties of location and crude methods of working which were adopted at the time this property was opened fifteen years ago, there would have been a generous profit to the owners.

To-day the location and the certainty of very large bodies of copper-bearing ores in this section must have a positive influence in determining new ventures, and sufficient capital, with the latest practice in metallurgy, must win for the fortunate owners such returns as will recompense them for the long period of idleness.

In 1866 extensive operations were carried on in Fannin county, Ga., the ores of this section resembling somewhat the slaty ores from the East Tennessee mine to the northward. They were worked from beds twenty feet wide over quite a length, but are now filled with water and debris to an extent which makes it impossible to judge of the real values. Concentrating and smelting operations were carried on for several years, as evidenced by the dumps now overgrown and changed by atmospheric agencies.

Just over the boundary line of Tennessee, and in the southeast corner of that State the Ducktown mines are found in a basin perhaps twenty miles in diameter, seemingly the issue of and formed by the partings and dislocations of the main chain of the Alleghanies, which at this point almost abruptly end their direct course and part to the east and west.

Entering this valley, by means of a winding trail over the towering mountains to the eastward, there is presented a picture of mournful strength and lifelessness, strangely impresssive in every sense—a desolate valley with its irregular placed knobs of vary-colored rocks, mineralized and artificial openings, denuded of all vegetation by the scouring action of sulphurous gases which swept over it for many years.

Rising 200 feet and upwards above the water level of the basin, with millions of tons of iron ores on the surface, these deposits sink into insignificance all known mining sections with the single exception of the central portion of the Sierra Morena in Spain. Every evidence of a wonderful concentration of mineral wealth at this particular location can be gained by cursory examinations, as nothing on the surface, neither tree nor vegetation, obstructs the general observation or renders difficult the closest study.

The rocks have been fairly scoured by the action of sulphur gas; numerous openings are found above the water level; enormous dumps of low grade ores and waste matters are met with on every side, and the wrecks of the earlier attempts in metallurgy are yet present to serve as milestones in the pathway of American progress.

Students in geology, mineralogy and metallurgy cannot afford to miss the rare treat of a visit to this well-known, but generally inaccessible location, and especially so before the march of newer events shall have taken from it the charm of silence and the ma-

jesty of a repose seen in no other mining region. Three parallel zones of minerals are fully proved over several miles in the central portion of the basin.

The East Tennessee, London, Cocheco and Hiwasse mines comprise the Western zone; the Isabella and Eureka range of deposits are in the center; the Polk county, Mary and Callaway mines are on the Eastern zone. Siliceous and slaty ores predominate on the Western zone, and this class of products require concentration by the usual methods employed in foreign countries where for more than 100 years they have been working out these problems.

The entire surface of the beds above the level of the streams are composed of limonites—altered by atmospheric agencies and the presence of percolating waters—the copper from which is found in pockets and masses generally, and is known by the term "black oxide."

This is easily soluble after contact with the air, and gives rise to the strong copper waters found in every mine, as well as overflowing into the streams near at hand. Immense amounts of cement copper have been made from these waters, and the actions are at all times going on underground, converting the sulphides of the ores into oxides, sulphates, etc., there being heat enough from this cause to be appreciable in winter, the snow melting from the surface in an exceedingly short time and before it is affected on any other part of the lands about.

Operations on a very extensive scale, covering a period of perhaps twenty years, have disclosed the general shape and extent of the lenticular beds in each of the mines named, and, with the single exception of the East Tennessee mine, there have been few developments at depths which prove values, the surface oxidized ores and higher grades of yellow sulphurets with black oxides of copper being alone worthy the exploitation when transportation charges were so excessive. With the system at present pursued in other mining districts modified to meet the particular necessities of each mine, this region should support a large and prosperous population for centuries with established industries needed by the contiguous agricultural and manufacturing centers.

[TO BE CONTINUED.]

THE CHEMICAL ANALYSIS OF ALUMINUM.

By Alfred E. Hunt, Geo. H. Clapp, and James O. Handy.

The principal impurities found by us, in commercial aluminum, have been silicon, iron, and copper.

The present system of valuation of aluminum is based, chiefly, on the *total percentage* of *impurities*, but account is also taken of their *nature* and *relative amounts*.

SOLUBILITY OF ALUMINUM.

Hydrochloric acid (sp. gr. 1.2) dissolves aluminum, in the form of drillings or chips, with very great rapidity. Sudden foaming up takes place, and much heat is produced. As this foaming often causes overflow, it is desirable to use a more dilute acid for analytical work. A mixture of 35 per cent. hydrochloric acid (sp. gr. 1.2) and 65 per cent. of water is better suited for general work.

Nitric acid (sp. gr. 1.42) when cold, appears to have no action on aluminum. In boiling acid, however, the metal is very slowly dissolved.

Nitric acid (sp. gr. 1.2), similarly, has little or no action when cold. At the boiling point, it dissolves aluminum slowly.

Sulphuric acid (sp. gr. 1.84), acting on aluminum, in the cold, soon forms on its surface a coating of sulphate, which protects the remaining metal. When heated, concentrated sulphuric acid dissolves aluminum slowly.

Dilute sulphuric acid, containing 25 to 50 per cent. of concentrated acid, dissolves aluminum, in the cold, but only after a long time. Heating hastens the solution to such an extent that we have hopes of using this method of attack in determining iron hereafter.

Aqua regia, even that which contains only one-sixth as much hydrochloric acid as nitric acid, and a volume of water equal to that of the mixed acids, dissolves aluminum *almost completely* without warming and *fully* when heat is applied.

Potassium hydrate solutions of various strengths dissolve aluminum readily.

F. Regelsberger (*Zeit. für angewandte Chemie*, June, 1891) uses potassium hydrate, usually in 40 per cent. solution, as a solvent in

the processes by which he analyzes aluminum. 1 gm. of aluminum requires for solution about 15 cc. of the 40 per cent. KOH.

We do not favor this solvent for general work. Its use prolongs the analysis, and renders close attention a necessity. The fatal objection, however, to its use in a laboratory, where large numbers of aluminum analyses are to be made, is its expense. It would cost three times as much as the acid processes which we employ.

SILICON.

a. Properties of Silicon in Aluminum.—In planning a method for determination of silicon in aluminum, it is necessary to remember that it exists therein, in two forms, the graphitoidal or crystalline, and the combined form.

PROPERTIES OF GRAPHITOIDAL SILICON.

When commercial aluminum is dissolved in any acid or mixture of acids, graphitoidal silicon remains behind, mixed with more or less silica. Our experiments show that this graphitoidal silicon has the following properties:

a. It is oxidizable only to a slight extent by heating over a Bunsen burner or blast lamp. Oxidation proceeds slowly even if the mass is frequently stirred.

We found that 0.1114 gms. of a mixture of silicon with a very small amount of silica gained .0050 gm. in 1 hour, over a Bunsen flame.

In a second experiment, 0.0908 gm. of a mixture of silicon and silica (half and half) gained .0018 gm. in fifteen minutes, heating over a blast-lamp.

Oxidation by heating alone is, therefore, too slow to be of use analytically.

b. Graphitoidal silicon is gradually oxidized and dissolved by heating with 40 per cent. potassium hydrate solution.

c. Fusion with sodium or potassium carbonate or nitrate, quickly oxidizes graphitoidal silicon and produces the corresponding silicate.

d. Notwithstanding the difficulty of oxidizing graphitoidal silicon *completely* by heating it in the air, its *partial* oxidation, by this means, is sufficient to interfere seriously with any method

which depends for success on its permanency, even for a short time.

Thus, when at the end of the first step in the determination of total silicon, we obtain a mixture of silicon and silica, it would seem to be a very simple procedure to treat this weighed mixture with a few drops of sulphuric acid and 3 to 5 cc. of hydrofluoric acid, evaporate, ignite, and weigh the *residual silicon.*

Unfortunately, as the experiments show, the determinations are not so simple. Of course, all the silica which was originally present, has been volatilized by the hydrofluoric treatment, but we have left, a *residue of silicon and silica* from the oxidation of a part of the original graphitoidal silicon. Having thus discovered that part of the graphitoidal silicon has been oxidized, we are left in doubt whether some silica from that source also has not been volatilized by the hydrofluoric acid treatment. Our experiments show that it has.

Thus, the apparent loss of weight by the HF treatment is made up of silica (originally present), plus silica from oxidation of graphitoidal silicon, and minus oxygen taken up by graphitoidal silicon. Table 1 gives the results of experiments by this method, *first* on the original mixture of silicon and silica, and *then* on the residues from the H_2SO_4 + HF treatment of the mixtures.

TABLE I.

Separation of Silica from Silicon by Sulphuric and HF Treatment.

	No. 491.	No. 483.	No. 499.	No. 602.	No. 475.	No. 475.	No. 475.
	Gms.	Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
Original weight silicon and silica	.0218	.0341	.0183	.0132	.0909	.0908	.0297
Loss of weight by first HF treatment	.0029	.0136	.0051	.0041	.0453	.0460	.0147
Loss of weight of first residue by HF treatment	.0039	.0067	.0020	.0004	.0094	.0167	.0061
Loss of weight of second residue by HF treatment		.0057	.0021	.0009	.0097	.0098	

Thinking that better results might be obtained by washing the silicon out of the mixture, by the use of dilute hydrofluoric acid alone, a few experiments were made. The weighed mixture of

silicon and silica, in a platinum crucible, was stirred with 5 cc. of Baker & Adamson's C. P. hydrofluoric acid, till lumps were disintegrated. Two parts of water were then added, and the mixture filtered. One wash was given with a mixture of 30 per cent. hydrofluoric acid and 70 per cent. water, and then a number of washings with water sufficient to remove the acid. The filter paper was then burned off and the residue weighed. Repetition of the washing, etc., showed that the graphitoidal silicon had been oxidized to a slight extent during the short heating required to burn off the filter paper.

TABLE II.

Separation of Silica from Silicon by HF wash.

	No. 419.	No. 427.	No. 443.
	Gms.	Gms.	Gms.
Original weight of silica and silicon	.0454	.0561	.0492
Loss of weight by first HF wash	.0094	.0123	.0120
Loss of weight of residue from first treatment by second HF wash	.0027	.0018	.0011

It is probable that the oxidation of the residual graphitoidal silicon can be wholly avoided by drying it on a weighed filter instead of attempting to burn off the filter paper, but we found that this would be impracticable for general work, because of the difficulty of weighing a number of filters under exactly the same conditions before and after HF washing.

We are now preparing to test for a method of filtration of the silica and graphitoidal silicon upon a platinum filter made in the form of a truncated cone, which will fit closely in the base of a platinum Gooch filter, or in such a filter, without the perforated base. The scheme being to weigh the filter after washing the silica and silicon mixture with hot dilute hydrochloric acid and water, and finally with hot water and drying at 80 degrees C., treating with hydrofluoric acid and sulphuric acid to dissolve the silica. Wash with hot water, and weigh again without delay, after drying at 80 degrees C., the loss in weight being the silica in the mixture, and the residue being the graphitoidal silicon. This method bids fair to prove approximately accurate. The platinum truncated cone is being made as an enclosed box of platinum sheet

soldered around a mass of an alloy of platinum and zinc, the top and bottom surfaces being perforated with fine holes for the passage of the liquids through it, the zinc being dissolved out of the alloy with sulphuric acid, leaving the interior of the cone a mass of platinum sponge to act as a filter. The filter can be cleaned from the graphitoidal silicon by immersing it in a mass of molten sodium carbonate in a platinum crucible, which will transform the silicon into silica, in which condition it can be washed out with hydrofluoric acid.

COMBINED SILICON.

A portion of the silicon in aluminum exists in the combined form.

The ratio of combined to graphitoidal silicon is, according to our experience, less, the more silicon the metal contains.

DETERMINATION OF TOTAL SILICON.

0.9334 gm. of thin turnings or drillings are placed in a 4-inch evaporating dish. 15 cc. of nitric acid (sp. gr. 1.2) and 2 cc. of concentrated hydrochloric acid are added and mixed, and the dish covered with a glass.

Solution takes place with evolution of NO_2 (hyponitric) fumes, showing that the conditions favor oxidation of combined silicon. In a few minutes, when action has nearly ceased, about 2 cc. more of concentrated hydrochloric acid are added. This completes the decomposition of all except the very pure grades of aluminum. These require warming with the acid mixture for a time.

After the aluminum has dissolved, 20 cc. of concentrated sulphuric acid are stirred in and the mixture evaporated quickly, on a hot plate, till it gives off fumes of sulphuric anhydride. The dish is removed before the aluminum sulphate separates and spirts.

After allowing it to cool for a few minutes, 75 cc. of water and 10 cc. of hydrochloric acid are added to the contents of the dish, and the whole well stirred. After boiling up for about 5 minutes, filter off the mixture of silicon and silica and wash with water, next with hot hydrochloric (30 per cent.) acid, and finally with water till free from acid.

The filter paper is then burned off and the residue fused with

about 3 gms. of sodium carbonate or fusion mixture. Cool the crucible containing the fusion by placing it in 25 cc. of water in a 4-inch evaporating dish. Cover the dish, and add sufficient concentrated hydrochloric acid to decompose the fusion; when effervescense ceases, rub, and wash silica off from surfaces of crucible and cover, and remove the latter from the dish.

Add 15 cc. concentrated sulphuric acid, and boil down the mixture to sulphuric fumes, on the hot plate.

After cooling sufficiently, add 75 cc. of water and 10 cc. of concentrated hydrochloric acid, boil up and filter. Wash thoroughly with water, 30 per cent. hydrochloric acid, and finally water. Burn off and weigh silica. As 0.9334 gms. of aluminum were taken for analysis, the weight of silica in grams less the silica obtained from the fusion mixture divided by .02 equals per cent. of silicon (total). We have many times treated with HF silica thus obtained and have always found it pure.

Our reasons for using sulphuric acid to dehydrate the silica are its rapid action compared with evaporation to dryness, and its leaving the silica in a form which filters easily. Evaporation of hydrochloric and nitric acid solutions to dryness fails to fulfil these requirements.

DETERMINATION OF IRON AND COPPER.

1 gm. of aluminum is dissolved in 40 cc. of a mixture of 33 per cent. concentrated hydrochloric acid with 67 per cent. water. When solution has been effected, boil up, dilute with warm water to 250 cc. and pass sulphuretted hydrogen into the solution, till saturated.

Filter off silicon, sulphide of copper, etc. The copper is separated from the residue and determined by any of the well-known methods. For instance, having obtained the copper in nitric acid solution from the ignited residue in which the silica has been rendered insoluble, the latter solution can be evaporated to dryness, and after ignition the residue of cupric oxide weighed. The copper may also be determined by battery precipitation from a dilute sulphuric acid solution.

The iron, in the filtrate, from the precipitation with H_2S, is estimated by titration (after boiling down the solution to 50 cc.) by means of standard potassium bichromate. We use stannous chlo-

ride to reduce the Fe_2Cl_6 and mercuric chloride to take up the small excess of stannous chloride.

The metallic aluminum is usually obtained by difference, in our commercial work, as we find that commercial metal made by electrolysis of alumina dissolved in molten fluoride salts, very rarely contains any solid impurities other than silicon, iron and copper. In some cases, we have found sodium or potassium present, which we have separated and determined as in well-known methods of analysis for the alkalies in fire clays.

DETERMINATION OF ALUMINUM

The determination of aluminum in the commercial metal by difference, is only approximate, for not only may there be alkali metals, but considerable amounts of occluded gases present to cause erroneous results, as well as the errors in determining the amounts of silicon, copper, and iron present.

In all important work we determine the percentage of metallic aluminum gravimetrically by precipitation, with hyposulphite of soda. The details of the method are as follows:

1 gm. of aluminum is dissolved in about 25 cc. HCl (35 per cent. strong acid) and evaporated to dryness. It is then redissolved in dilute HCl by boiling, and is filtered from silica and silicon. The filtrate is diluted, warmed, and saturated with H_2S. CuS is filtered off and washed with H_2S water. The filtrate is boiled till free from H_2S and made up to 250 cc. 50 cc. of this solution are nearly neutralized with NH_4OH. Then 5 cc. of saturated ammonium phosphate and 10 cc. saturated sodium hyposulphite are added and the solution boiled till free from SO_2.

Filter and wash with hot water. Redissolve the $AlPO_4$ in dilute HCl, reprecipitate with slight excess of ammonia and a little phosphate and boil.

Filter, wash, ignite in porcelain and weigh as $AlPO_4$ containing 22.5 per cent. aluminum.

TITANIUM AND CHROMIUM ALLOYS

Titanium and chromium are added to aluminum to give hardness and resilience to the metal. Chromium gives the best results for hardness in castings. Titanium imparts more toughness and

resilience, and is added when the metal is to be worked after being cast.

DETERMINATION OF CHROMIUM IN CHROMIUM-ALUMINUM ALLOY.

2 gms. of chromium-aluminum alloy are treated in a 5-inch porcelain dish, with about 50 cc. of 10 per cent. KOH solution. When action has slackened, the solution is boiled up, and finally filtered. The washed residue contains the chromium, together with some silicon, silica, iron, aluminum hydrate and titanium, if present.

Burn off the filter paper in a porcelain crucible; transfer the residue to a large platinum crucible, and treat with 1 cc. concentrated H_2SO_4 + 5 cc. HF. Evaporate to SO_3 fumes; add 4 gms. bisulphate of potassium; cover the crucible and fuse, for about 20 minutes, at a low temperature. Finally heat to a high temperature over the blast-lamp, to expel nearly all the free acid. Cool a little, and add sufficient Na_2CO_3 to make alkaline; also a little KNO_3, and fuse.

Dissolve in hot water and filter. Filtrate contains all the chromium as chromate, together with some alkali aluminate and silicate.

Decompose the latter by warming the solution with NH_4Cl, and filter.

Reduce the chromium in the filtrate, by sodium sulphite or sulphurous acid, and precipitate the chromium as hydroxide by means of ammonia, as usual.

Re-dissolve the $Cr_2H_6O_6$ in HCl; dilute and re-precipitate with ammonia, to free from alkali, taking the usual precautions as to washing free from chlorides in each case.

Weigh as Cr_2O_3.

If the intermediate fusion with bisulphate is omitted, some chromium will not be oxidized.

METHOD OF ANALYSES OF TITANIUM-ALUMINUM.

2 gms. of the alloy in a porcelain evaporating dish (5 inches in diameter and covered by a watch glass) are dissolved by gradual addition of 50 cc. of "potash solution" (100 gms. KOH in one

liter distilled water). Boil for 10 minutes to insure complete solution. Dilute with distilled water to about 125 cc. Boil up and filter as quickly as possible, washing ten times with boiling water. This filtration separates the iron and titanium quite completely from aluminum. Burn off the residue in a porcelain crucible. Crush it in an agate mortar, and mix with about 8 gms. (6 gms. first, then 2 gms. later) of pure bisulphate of potassium. Fuse in a thin walled platinum crucible of about 40 cc. capacity. The cover of the crucible should fit well.

During the first 15 minutes, the crucible should be on a platinum wire triangle over a small flame of a Bunsen burner. The burner flame should be protected from draughts by a sheet iron chimney, and the flame at first should just touch the crucible bottom. At intervals of 5 minutes, remove the cover, carefully invert it (without losing the drop of $KHSO_4$), and place it on a clean stone surface. Then give the contents a rotating motion holding the crucible firmly in the tongs. At the end of 15 minutes turn up the light till the lower one fourth of the crucible is red hot; agitate frequently as before. In ten minutes more, turn on flame full and heat for five minutes with shaking. Cool, add 2 gms. more $KHSO_4$, and gradually bring to a homogeneous fusion, but do not heat long enough to drive off much free SO_3.

Pour out the liquid fusion into a warmed and dry platinum dish after the cake cools it will not adhere to the dish. Place it together with the crucible and cover in a 250 cc. beaker. Add 150 cc. of water, heat to and keep at 40 degrees C. with occasional stirring until all soluble matter is dissolved. Filter rejecting the residue, if any, on ignition and treatment with HF show it to be only SiO_2. If it contains anything, fuse once more with $KHSO_4$ again.

ESTIMATION OF TITANIUM

The filtrate contains all the TiO_2 and Fe_2O_3. Add dilute NH_4OH to slight precipitation and redissolve by stirring. Add dilute (1:3) H_2SO_4 until this precipitate just redissolves. Add 4 drops of concentrated H_2SO_4, then dilute to 250 cc., and saturate with sulphur dioxide. Heat slowly to boiling and boil gently for five minutes. Add a little strong SO_2 water as usually to keep the iron in the ferrous state. Fil

ter through double-washed filters, and wash with hot water. Ignite in porcelain crucible over blast-lamp.

Weight of $TiO_2 \times .60 = Ti$.

ESTIMATION OF IRON.

In the filtrate from the TiO_2, the Fe is oxidized, precipitated by NH_4OH, filtered and washed, re-dissolved in HCl, and titrated with bichromate. Do not weigh the Fe_2O_3 and Al_2O_3 as precipitated. Attempts to titrate the iron in the sulphate solution occasionally give results which are not accurate.

ESTIMATION OF SILICON IN TITANIUM-ALUMINUM ALLOY.

Silicon is estimated just as usual, except that we use a little more HCl (20 cc.) in re-dissolving after evaporation with H_2SO_4. Under these conditions, no TiO_2 remains with the silica, although it is best to test it, always, with HF and H_2SO_4.

A RAPID DIALYZER.

By C. E. Linebarger.

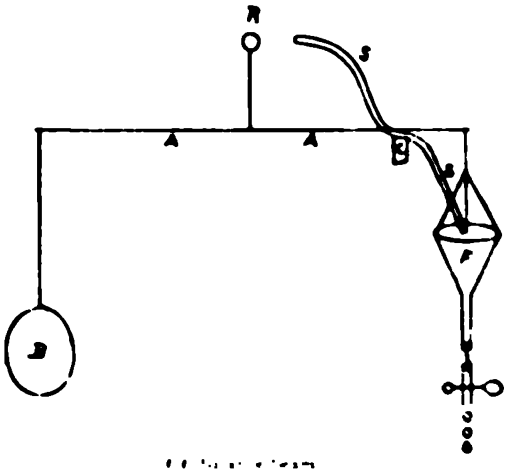
The rapidity of dialysis depends upon the extent of the surface of the dialyzing membrane and the difference of concentration of the solutions separated by it. The two requisites of an efficient and rapid dialyzer are then: 1, A dialyzing membrane presenting as large a surface as possible; 2, A frequent renewal of the outer liquid, so as to keep the difference of concentration as great as possible.

The following apparatus meets these two requirements very well, and, at the same time, has the advantage of consisting of parts that can be found in any laboratory, no matter how small its equipment may be.

A funnel of any size is fitted with a filter *folded in plaits* made of parchment paper. The paper, cut into a circle of suitable size, is first thoroughly wetted with water, so as to enable one to fold it evenly. Into the stem of the funnel is inserted a perforated cork, through which passes a tube. Over the lower end of the tube is slipped a bit of rubber tubing, which can be closed with a pinch-cock. The solution to be subjected to dialysis is put into the parchment paper, and the space between the folds of the paper and the glass funnel filled in with water. The funnel is supported in

the ring of a retort stand, and the whole set in a warm, quiet place. At any time, when it may be judged desirable, by opening the pinch-cock the "diffusate" may be drawn off, and then replaced by pure water. Thus the difference of concentration may be kept as great as possible.

The apparatus may be made to work automatically by a very simple contrivance, i. e., a constant stream of water may be passed through the space between the parchment paper and the funnel, which carries off everything diffused. The funnel is balanced at one end of a rude balance beam. A tube conducts a stream of pure water from a reservoir into the funnel, i. e., the space between the funnel and the parchment paper. This tube passes around under the balance beam over an independent support, so that if the beam be thrown out of equilibrium from the funnel and its contents becoming too heavy, it will be pinched close, and the flow of water will cease. By letting the pinch cock closing the stem of



the funnel remain a little open a stream of water of any degree of rapidity may be run in. As soon as the funnel becomes a little light the pressure on the tube from the reservoir is removed and water flows in. The apparatus when once regulated,

will continue to work indefinitely. The results obtained with an apparatus of this kind are very satisfactory. I am carrying out some quantitative experiments with colloid solutions of compounds, such as molybdic and tungstic acids, with a view to ascertain exactly the relation of the rapidity of dialysis obtained with the old-fashioned form of dialyzer and the one described above.

CHICAGO, ILL.

THE USE OF ASBESTOS IN FILTRATION.

BY W. P. BARBA.

In the usual manner of determining manganese by Ford's admirable method, a great deal of time is used up in avoiding the difficulties introduced by the silica present in the steel or iron. The solution of the drillings in HCl, the expulsion of the HCl by HNO_3, and the tedious filtration on the pump, may all be avoided by the use of finely divided asbestos in HNO_3, as pointed out by me in the filtration of carbon sponge (this Journal **5**, 596).

The asbestos is best prepared by triturating in a porcelain mortar to moderate fineness, washing with HNO_3, and may be kept suspended in strong HNO_3 for use. The method as now practised at Midvale may readily be carried through in forty minutes, and is as follows:

5 gms. of steel are dissolved in 80 cc. HNO_3, sp. gr. 1.20 and boiled to one-half that bulk. 75 cc. of strong HNO_3 are then added, and boiled for about five minutes more. The usual portion of $KClO_3$ is added—about 5 gms.—and the solution boiled till precipitation is effected. The beaker is then withdrawn from the plate and a quantity of finely divided asbestos in HNO_3 is added. The solution, when sufficiently cooled, is filtered on a tight asbestos plug, washed twice with HNO_3, and then with water till all acid is removed. The plug with the precipitate is blown back into the same beaker, ferrous sulphate added, and the titration carried out as usual.

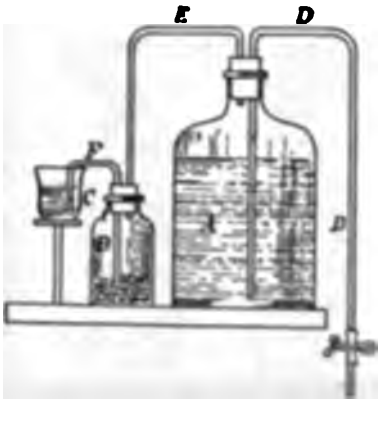
It will be found that filtration is very much facilitated by the presence of the fine asbestos, and that the solution of the precipitate in the $FeSO_4$ is almost instantaneous, thus removing the difficulties of the two most tedious operations of the method.

LABORATORY OF THE MIDVALE STEEL COMPANY.

VOLUMETRIC DETERMINATION OF IRON WITH BICHROMATE OF POTASH AND STANNOUS CHLORIDE

To avoid the tedious and troublesome method of getting the end reaction by adding a drop of the solution to a drop of ferrocyanide of potassium after each addition of bichromate, the author proposes to add to the solution of the ferrous salt, at once, an excess of bichromate, and titrate back with stannous chloride. To get the end reaction he uses a drop or two of iodine and the same amount of starch solution and claims that upon adding the solution of stannous chloride, the excess of bichromate is deoxidized first, then the iodide of starch, and finally the ferric chloride. The disappearance of the blue color of the iodide of starch is the indication of the end reaction showing the amount of stannous chloride necessary to reduce the bichromate. On account of the presence of the chromium salt the liquid does not become colorless but remains a bluish green color, but if the liquid is sufficiently dilute the disappearance of the iodide of starch color is sharp and most easily seen. The bichromate solution is prepared by dissolving 6 gms. of bichromate of potassium in 1 liter of water, the stannous chloride solution by dissolving 6 gms. of pure tin in hydrochloric acid and diluting to 1 liter. The stannous chloride solution should be very acid. These solutions correspond almost exactly, 1 cc. of stannous chloride reducing 1 cc. of bichromate.

To standardize the solutions take a measured volume of the bichromate solution, add a drop of iodine solution and one of starch solution and drop in the stannous chloride solution from a burette until the blue color of the iodide of starch disappears; this gives the value of the stannous chloride solution in terms of the bichromate. Dissolve a weighed amount of pure iron in hydrochloric acid out of contact with the air, dilute, add a measured volume of bichromate solution sufficiently large to oxidize the iron

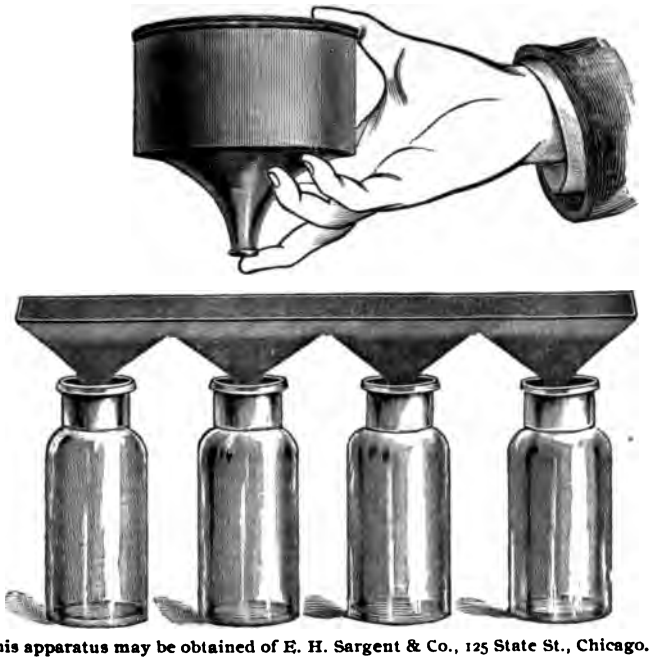


and have an excess of bichromate, then titrate back with the stannous chloride. The author suggests a piece of apparatus for keeping the solution of stannous chloride. The bottle *A* contains the standard solution, which is drawn off by the syphon *D*. The tube *E*, ending just below the stopper, connects the bottles *A* and and *B*. *B* contains marble in lumps, and the beaker *C* dilute hydrochloric acid. When by the action of the syphon *D* a partial vacuum is formed in *A*, the acid is drawn from *C* through *F* into *B*, and the carbonic acid generated produces a pressure in *A* and *B*, supplying the place of the liquid drawn from *A*, and eventually forcing the hydrochloric acid back into *C*.—*Rodolfo Namias, Gazz. Chim. Ital.*, 1891, p. 473. A. A. B.

MIXER AND DIVIDER FOR ORE SAMPLES.*

By H. L. Bridgman.

This apparatus entirely obviates the tedious and frequently inaccurate methods (usually with oil cloth and spatula) now in general use, for mixing and dividing the ground samples of ore, matte,



*This apparatus may be obtained of E. H. Sargent & Co., 125 State St., Chicago.

slag and other similar material. An experience of several months has shown a very decided improvement in accuracy, speed, and general convenience over the old way.

The operation is as follows: The ground material is introduced into the large, covered funnel, (mixer,) the outlet being first closed by thumb or finger, as may be most convenient. Funnel and contents are then well shaken for a few minutes, and then, with opened outlet, passed to and fro over the set of distributing funnels (divider) and bottles as shown. With very finely ground or very light material the flow may be assisted by a slight shaking or tapping with the hand. The little skill necessary is readily acquired.

The mixer will also be found very useful for the prompt and thorough mixing of crucible assay charges, and all other work of similar character.

To test the efficiency of the mixer, a lot of 6 assay tons of litharge, 3 assay tons of soda and ¼ assay ton of argols was taken well shaken, divided by weight into three lots of 3¼ assay tons each, and these charges fused separately in crucibles. The resulting lead buttons weighed

55.450 gms. 55.416 gms. 55.398 gms.

ORE SAMPLING MACHINE.*

By H. I. Bateman.

This machine is a modification of the large machine which is doing excellent work. Its particular field of usefulness is the quick and certain cutting down of the miscellaneous small samples—from five pounds to five hundred pounds in weight—that are constantly being received by all assay offices. It will handle anything from the finest assay pulp to crushed material of one-half inch or more in size. It is a very decided improvement over any of the present methods of quartering or cutting down with sample shovel or tin sampler.

Method of operating. The material is fed either by hand or (with large lots) from a suitably supported bucket into the funnel (F) the divider (D) being first set in rotation by hand (clock

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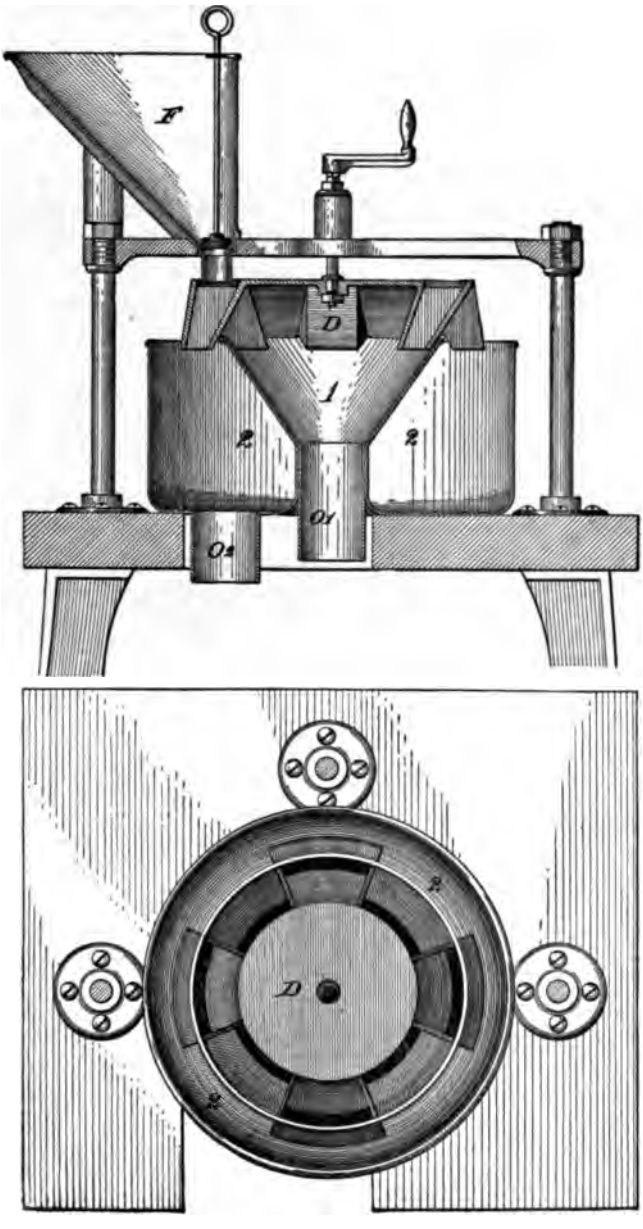

F
D
I
R
R
O1
O2
R
D
R

work or any convenient power. The divider gives, as will be seen by inspection of the drawing, eight cuts to the revolution, four being delivered to the funnel 1, and four to the receptable 2; that is with uniform flow and speed, cutting the material in half. The divider may easily run 100 revolutions per minute, giving in that time 800 cuts, a very much greater distribution and division than can be secured in any other way. The rejected sample passes down the outlet to "O 2," both into suitable vessels. The retained portion, should it be too large, may be cut again, and again, until of suitable size. The operation is very accurate and very rapid, being about as fast as the material will flow through a one-inch spout.

TITRATION OF ZINC WITH POTASSIUM FERROCYANIDE IN AN AMMONIACAL SOLUTION

A 4 per cent. solution of copper sulphate is prepared, and with this solution a strip of filter paper, very white and smooth, 5 cm wide, is marked longitudinally by means of a hair pencil, and dried quickly over the flame. Cross sections of this strip, carefully kept in a stoppered bottle, are used for an indicator. A drop of the precipitated solution of zinc let fall upon the white end of such a slip, soon travels to the blue part, and if there is an excess of ferrocyanide, a red or reddish streak will appear. 0.1 to 0.2 cc. of a decinormal solution of ferrocyanide in 100 cc. of ammoniacal water, quickly and certainly showing. The standard solution of ferrocyanide is so adjusted that 1 cc. equals 0.005 gms. zinc. Potassium ferrocyanide thus prepared is at first almost colorless, but soon turns to a gold yellow, and after a long time deposits a small quantity of ferric oxide. If the solution, however, is preserved in dark glass bottles, and 1 to 2 gms. caustic potash per liter is added this change is avoided.

In the presence of manganese and magnesia, the author uses the following method: 2.5 gms. of the ore are dissolved in hydrochloric acid, and diluted to 250 cc. After rinsing a burette carefully with some of this solution, 50 cc. are poured in and 5 cc. are run out into a small flask. 10 cc. ammonia and 5 cc. of ammo-

nium carbonate solution, (containing 5 gms. solid carbonate, 5 gms. sal-ammoniac, and 10 cc. ammonia per 100 cc. of the solution) are added. After heating until the dense precipitate settles, it is set aside to cool. Meanwhile 25 cc. of the original solution are run from the burette into a beaker with 10 cc. ammonia, and the amount of ferrocyanide is determined to 1 cc. 25 cc. more of the original solution are then titrated accurately. To the ammoniacal solution in the flask, which was allowed to cool, 1 or 2 cc. of a ten per cent. ammoniacal sodium phosphate solution are added, and after the manganese and magnesia have been filtered off, the solution is titrated. Manganese may be titrated by ferrocyanide, if no other bodies are present which are precipitated by the same reagent. For this determination, a measured quantity of a decinormal ferrocyanide solution is mixed with sal-ammoniac and ammonia, and the faintly acid or neutral manganous solution is dropped into the ferrocyanide until the reaction on the slip of copper sulphate test-paper just ceases to appear.—*F. Moldenhauer, Chem. News* **64**, *150*; *Chem. Zeit. and Zeit. anal. Chem.* A. H. W.

THE QUANTITATIVE DETERMINATION OF SULPHUR.

The process which the author describes renders it possible to expel the sulphur from *insoluble* sulphides as sulphuretted hydrogen, when any of the standard methods may be applied. To accomplish this, he mixes the sulphide with an excess of iron, then heats the mixture in a glass combustion tube for five to ten minutes to dull redness in a current of dry carbonic acid, when the ferrous sulphide, thus formed, when cold, may be readily decomposed by hydrochloric acid. The iron used is the ordinary "ferrum reductum," which is first ignited before using in a current of dry hydrogen. A blank determination is first made of the amount of sulphur contained in the reagents used, as follows:

Three gms. of iron powder are put in a porcelain crucible, which is supported upon a piece of sheet asbestos, having in the middle a hole exactly fitting the crucible. Heat is now applied until the crucible has been heated at a dull redness for ten minutes, in a current of carbon dioxide; when cold, still in a current of carbon

dioxide, the crucible is put into an Erlenmeyer flask, (400 cc capacity) having a two-holed cork. Through one opening, passes the gas delivery tube, provided with a small condensation bulb, above which it is bent downwards at an angle of 15°, so that its lower end reaches below the bottom of the flask. Through the other hole, passes a tube, surmounted with a globe funnel with a glass stop-cock. The lower end of the glass delivery tube is connected with a Kipp hydrogen apparatus, and a strong current of hydrogen is passed for five minutes, while the stop-cock of the funnel is left open. The stop-cock is then closed. Then the gas-delivery tube is connected with a Fresenius Volhard absorption apparatus. The first of the vessels is filled with 50 cc of the purest 2 per cent. hydrogen peroxide, and 10 cc of binormal ammonia, while the second contains 100 cc of ammonia of like strength, 100 cc of dilute hydrochloric acid (1:5) first boiled, are put into the globe funnel, and gradually allowed to enter the flask. The evolution of gas at once commences, and is so regulated by heat that three or four bubbles pass every second through the absorbent vessels. In from 1½ to 2 hours, the evolution is completed when a current of pure hydrogen is passed for half an hour through the globe funnel tube. The contents of the absorbtion apparatus are poured into a beaker, covered with a watch glass, boiled for fifteen minutes, acidulated with hydrochloric acid, and evaporated to dryness in a porcelain capsule on the water bath. A few drops of concentrated hydrochloric are added to the dry mass, which is then dissolved in hot water, filtered and the sulphur precipitated in the filtrate with barium chloride.

In the actual analysis, a little of the iron powder is first placed in the decomposition crucible, then the substance, then some more iron powder, when the whole is thoroughly mixed with a platinum spatula. The mixture is covered over with iron powder, and the operation is conducted as in the blank experiment. This method is applicable to arsenic sulphides, but not to the technical analysis of pyrites, as the sulphur present in every combination is determined. In the case of arsenic-bearing minerals, the hydrogen arsenide evolved is passed, after the removal of the absorption vessels, into an ammoniacal solution of silver [illegible]

ON THE ESTIMATION OF SULPHUR.*

By George Craig.

Evolution methods, whereby the substance to be determined is first of all eliminated as a gas from the material under examination, must always be more satisfactory than gravimetric methods, although no greater degree of accuracy is attained thereby. Such, for instance, is the estimation of NH_3 by liberation with alkali, with subsequent condensation and titration with standard acid.

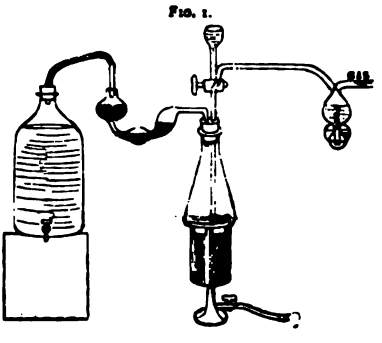
Sulphur, when it exists as monosulphide, decomposable by HCl, is certainly best determined after expulsion as H_2S.

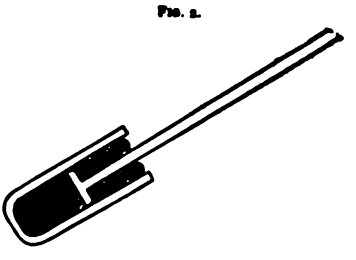
Pig-iron and steel, even when containing Cu, yield all their S as H_2S on treatment with HCl, which, as I proposed in 1881, may be completely oxidized to SO_3 by passing the gases through ammoniacal H_2O_2.

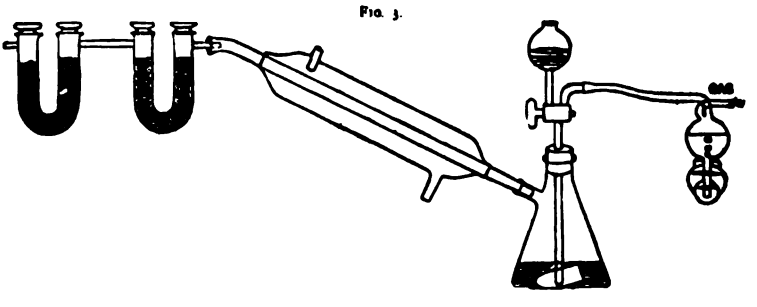
In blast-furnace slags the S exists wholly as CaS, which, it must be borne in mind, readily oxidizes when the finely ground slag, especially from hematite iron, is kept for any time. The only correct method whereby it can be estimated, unless with the expenditure of much time and labor, is by decomposing the slag with HCl and estimating the S in the H_2S evolved. For this purpose, I use the apparatus shown in Fig. 1, which scarcely needs explanation. 20 gms. of finely ground slag is heated with 1 oz. of boiled water, and the air expelled from the flask by a current of coal-gas which has been passed through a mixture of KHO and H_2O_2 in the Leibig's bulbs shown. When boiling agitate so that the slag is all in suspension, and add HCl by means of the 3-way stop-cock, continuing the agitation until the slag is all decomposed, which takes place in a few seconds; boil, and pass a current of the purified coal-gas through the apparatus with the aid of the aspirator. The nitrogen bulb—containing 100 gms. H_2O_2, 200 gms. NH_4HO—is preferably made, as in the figure, by cutting the escape-tube nearly at the bulb, widening the orifice, introducing some glass beads, and connecting with india rubber tubing as shown. The contents of the nitrogen bulb are washed into a small beaker, heated to boiling, acidified, and the SO_3 determined as $BaSO_4$ as usual.

*Chem. News 64, 266.

It is now more than a year since it occured to me that compound sulphides, such as pyrites, etc., might be made amenable to this evolution process also, by the simple preliminary operation of heating with zinc dust, and so reducing to the state of monosulphides. In a recent number of the *Chemical News* there is a translation from the *Berichte* of an almost identical process; * but as reduction with zinc is very much simpler, a description of the method I employed may be of interest.







Ordinary zinc-dust, after passing through a fine sieve, is heated to redness to expel moisture and occluded hydrogen, and allowed to cool out of contact with air; a tube of Bohemian glass closed at one end suits admirably for this purpose.

10 or 20 gms. of the pyrites in fine powder are weighed into a small ignition tube of Bohemian glass (2 inches long by ½ inch diameter), then five times its weight of zinc-dust added, intimately

*See Preceding Article.

mixed with a platinum wire, the surface leveled by tapping gently, and covered with a layer of zinc-dust. A stout glass rod, about 8 inches long, has one end flattened out into a disc that enters easily into the little decomposing tube. This is introduced until the disc rests lightly on the covering layer of zinc-dust, and the upper portion of the tube is packed with asbestos yarn firmly enough to enable the glass rod to serve as a support (Fig. 2). The tube and contents is then revolved over an argand flame until thoroughly heated, and then over a Bunsen flame. In a few seconds bright incadescence takes place, and after maintaining at a red-heat for thirty seconds longer it is withdrawn gradually, revolving all the while, and then allowed to cool.

When carried out in this manner practically no sulphate is reduced, but when maintained at a red-heat for 5 to 10 minutes all sulphates are reduced. Apropos of sulphates in pyrites, I have not seen it recorded that a considerable amount of pyrites may be oxidized while grinding the sample in the agate mortar; in the dark a red glow follows the track of the pestle.

After withdrawing the support and asbestos packing, the tube is dropped into a 4-oz. conical flask with side-tube, connected with condenser and U-tubes, as shown in Fig. 3. The first U-tube contains $CaCl_2$, and the second is filled with glass beads and contains 100 gms. of NaHO solution (1000 gms. NaHO and 1500 gms. water). 1 oz. boiled water is added, and a current of purified coal-gas passed through the apparatus. Heat is applied and the HCl gradually run in until decomposed, contents boiled, and apparatus washed out with a current of gas. I preferred to estimate the H_2S by washing out the U-tube (without removing stoppers) into a beaker, adding excess of $FeCl_3$, agitating, acidifying with HCl delivered at bottom of liquid by means of a pipette, heating until all FeS decomposed, and titrating with bichromate. The ideal process would be to accurately weigh the NaHO solution and titrate after absorption with acid, using an indicator neutral to NaHS or Na_2S. The arsenic I found was completely expelled, so that not a trace could be detected in the combined residues from a number of experiments.

LUGAR IRON WORKS, CUMNOCK, N. B.,
November 19, 1891.

THE DETECTION AND DETERMINATION OF POTASSIUM SPECTROSCOPICALLY.*

By F. A. Gooch and T. S. Hart

Bunsen and Kirchhoff originally determined the delicacy of the spectroscopic test for potassium by exploding in a darkened room a mixture of potassium chlorate with milk sugar, and observing the amount of finely divided chloride which it was necessary to diffuse through the given space in order to bring out unmistakably the spectrum of the metal. These investigators were able to state that the presence of no more than $\frac{1}{200}$ of a milligram of the potassium salt is sufficient to give to the flame the characteristic spectrum of the element. By similar methods, the delicacy of the tests for lithium carbonate and sodium chlorate were shown to be a thousand times and three thousand times as delicate respectively. Practically, the detection of lithium and sodium spectroscopically is extremely easy and satisfactory, the only difficulty being that the exceeding delicacy of the sodium test, and the ubiquitousness of sodium salts often make a decision doubtful as to whether that element is present essentially in the substance under examination or by accident. With potassium the case is different, and experience shows that, when the test is to be made for very small amounts of potassium, the simple method in vogue for developing the luminosity of lithium and sodium, the dipping of a single loop of platinum wire in the liquid or solid substance, and the placing of the loop in the Bunsen flame, fails, because, as it seems to us, so great a proportion of the material is dispersed before the heat of the flame effects the dissociation of the metal which precedes the production of the spectrum.

We have endeavored to improve the conditions of exposure of the test substance by making use of more powerful flames and by substituting for the single loop the hollow coils of platinum wire first recommended, so far as has come to our knowledge, by Trechotin in the description of a method for the quantitative determination of lithium. Such coils are easily made by winding the wire somewhat obliquely about a rod of suitable size, pressing the coils close together, and gathering the three coils into a twisted band

* [illegible]
[illegible] Read [illegible]

dle. The size of the coils is adjustable without difficulty, so that each coil may be made to hold almost exactly any appropriate amount, and to take up this amount with very little variation in successive fillings, provided only that the precaution be taken in the process of filling to plunge the coil while hot into the liquid, and to keep its axis inclined obliquely to the surface of the liquid while withdrawing it. How closely the capacity of such coils may be adjusted, and how uniformly they may be filled, is shown in the figures of the accompanying record.

	I.	II.	III.	IV.	V.	VI.
	Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
Weight of filled coil . . .	0.1996	0.2780	0.2794	0.2844	0.3572	0.3296
" " . . .	0.1996	0.2780	0.2794	0.2845	0.3571	0.3296
" " . . .	0.1996	0.2780	0.2794	0.2844	0.3572	0.3298
" " . . .	0.1996	0.2780	0.2794	0.2845	0.3271	0.3298
" " . . .	0.1996	0.2781	0.2794	0.2844	0.3571	0.3296
" empty coil . .	0.1986	0.2760	0.2764	0.2804	0.3521	0.3100
" contents (mean)	0.0010	0.00202	0.0030	0.00404	0.00504	0.01968

It is plain that we have in these coils simple means of taking up known amounts of material in solution; and by gentle heating the liquid may be evaporated and the solid material left thinly and uniformly spread, not easily detachable, and so in condition to be acted upon with effect when brought to the flame. The evaporation may be conducted with little danger of loss of material by holding the handle of the coil across the flame with the coil proper at a safe distance outside; but we have generally, and preferably, used a hot radiator over which the coils are exposed, the handles resting upon a flat asbestos ring. The burner which we have used in heating the coils before the spectroscope is of the Muencke pattern and gives a powerful flame 3 cm. wide at its base. We have generally adjusted the flame to a height of 20 cm., and have introduced the coil, after thorough drying, just within the outer mantle, on the side next the spectroscope, with the axis transverse to the slit of the spectroscope and the handle across the body of the flame. In cleaning the coils we have found it convenient to heat them in the flame of an Argand burner of the Fletcher pattern, beneath

which is burned, in a small lamp, alcohol containing about a twentieth of its volume of chloroform. The products of combustion of the alcohol and chloroform are conveyed to the interior of the flame above by a glass funnel fitted by a cork to the tube of the Argand burner. This arrangement of apparatus gives a hot colorless flame through which hydrochloric acid is constantly diffused in condition to clean the wires completely and without attention. The spectroscope which we have employed is a well made single prism instrument provided with a scale, and a movable observing telescope so that different portions of the spectrum may be viewed or cut off at will. The slit is adjustable, but for measuring its width we have been obliged to have recourse to the device of closing it upon wires of known gauge. Our work has been done in the ordinary diffused light of the laboratory, care having been taken to cut off from the room direct sunlight only; but in observing it has been our custom to shield the eye in use as completely as possible with the hand or with a dark handkerchief, and to cover the eye not in use. We have found it desirable to use the scale of the instrument illuminated to the lowest degree of visibility to aid the eye in placing barely visible lines.

Upon experimenting with the apparatus described, it was found that the largest coil used was best adapted to our purpose, and accordingly, in all the experiments made subsequently and recorded in the following accounts, coils holding [illegible] of a gm. of water measuring 2 mm. in diameter by [illegible] cm. in length, made of N[illegible] wire [illegible] mm. in diameter, and wound in about thirty turns, were the ones employed. With these coils and the flame adjusted to a height of [illegible] cm. we have been able to recognize the presence of potassium, taken in the form of the chloride, in a coil full of liquid containing [illegible] gm. of the metal in [illegible] when the slit had a width of [illegible] mm., and containing [illegible] gm. in the same volume of solution when the slit was set [illegible] mm. wide. That is to say, [illegible] mg. of potassium to the coil full produces a line distinctly visible with a slit of [illegible] mm., and [illegible] mg. with a slit of [illegible] mm., and it seems evident that this [illegible] method of producing the spectrum of potassium gives results of a delicacy approaching that indicated in the experiments of Bunsen and Kirchhoff.

These determinations were made with pure potassium chloride carefully prepared from the chlorate, but in practical analysis it almost always happens that sodium is also present. Experiments were therefore made to determine the influence of varying amounts of the latter upon the visibility of the potassium line. The dilution of the potassium chloride was adjusted nearly to the last limit of visibility, so that a coil-full of the liquid should contain $\frac{1}{700}$ mg., or $\frac{1}{1000}$ mg. of the element, according as the slit was 0.18 mm. or 0.23 mm. wide; to this solution were added weighed amounts of pure sodium chloride twice reprecipitated and washed by hydrochloric acid; and the spectroscopic tests were carried out as before, the sodium line being kept within the field of view with the potassium line.

Weight of K in a Coil-full.	Weight of Na in a Coil-full.	Ratio of Na : K.	Width of Slit.	Number of Trials.	Characteristic of Line.
Mg.	Mg.		Mm.		
0.0010	0.0000	0 : 1	0.23	3	visible
0.0010	0.0020	2 : 1	0.23	3	visible
0.0010	0.0100	10 : 1	0.23	3	visible
0.0010	0.0200	20 : 1	0.23	3	visible
0.0010	0.0400	40 : 1	0.23	3	visible
0.0010	0.0500	50 : 1	0.23	4	very faint or none
0.0010	0.1000	100 : 1	0.23	3	none
0.0010	0.2000	200 : 1	0.23	3	none
0.0014	0.0000	0 : 1	0.18	3	visible
0.0014	0.0560	40 : 1	0.18	3	visible
0.0014	0.0700	50 : 1	0.18	3	visible
0.0014	0.1400	100 : 1	0.18	2	visible
0.0014	0.1400	100 : 1	0.18	2	none

It is obvious from these results that a considerable amount of sodium may be present in the flame, when the sodium line is in full view in the spectrum, and the slit adjusted to nearly the lowest limit of visibility of pure potassium, without interfering with the appearance of the potassium line; but that a quantity of sodium amounting to a hundred times that of the potassium is sufficient to entirely overpower the spectrum of the potassium. The inference is plain that the proportion of sodium to potassium should

not be permitted to reach 100 : 1 when it is desirable to bring out the full delicacy of the spectroscopic test with the sodium line in the field of view. When too great a proportion of sodium is present, its influence may be moderated by throwing the sodium line out of view, if the instrument in use possesses the necessary adjustment; otherwise, it is easy to effect a partial separation of the sodium chloride from the potassium chloride, before bringing the solution to the test, by precipitating with alcohol. Our experience shows that the delicacy of the test for potassium is not impaired materially by such treatment of the mixed chlorides. We found, for example, that 0.0070 gm. of potassium chloride mixed with 0.5 gm. of pure sodium chloride, dissolved in the least amount of water and extracted carefully by about 7 cc. of absolute alcohol applied in successive portions, was so completely retained in solution and separated from sodium, that a coil full taken from the solution diluted to 140 cc. gave the spectroscopic test for potassium distinctly with the slit at 0.23 mm. In this case, at least, the treatment did not diminish the delicacy of the test, for a coil full of the diluted solution could not have contained more than [illegible] mg. of potassium, if nothing had been lost. It was found, in like manner, that, by taking pains to evaporate the alcoholic extract and to dissolve the residue in a drop of water, 0.0001 gm. of potassium originally present as the chloride with 0.5 gm. of sodium chloride was easily found. By turning the observing telescope so as to cut off as completely as possible the sodium light we were able to detect potassium in four successive tests of a drop of the final solution which was just large enough to fill the coil four times, when the original amount of potassium present with 0.5 gm. of sodium chloride was 0.0001 gm. This is equivalent to detecting [illegible] mg. of potassium in a drop large enough to fill the coil once. We were assured of the entire absence of potassium from the sodium chloride which we used by the fact that the similar extraction of 1 gm. of the salt by alcohol left a residue which yielded no line of potassium when examined spectroscopically. It is perhaps worth noting in passing that the coil may be made to pick up a drop of a size only sufficient to fill it by simply touching the coil while hissing hot to the drop.

Certain experiments in which the method of manipulation which

we have described was applied to the determination of potassium salts other than the chloride indicated that the test is less delicate in the case of the sulphate, and rather more delicate in the case of the carbonate. We were able to find the red line of potassium unmistakably, when only $\frac{1}{2000}$ of a milligram of potassium was introduced into the flame in the form of the carbonate.

The quantitative determination of potassium by the spectroscope has never, so far as we know, been accomplished heretofore. Sodium appears to have been successfully estimated by Champion, Pellet and Grenier* by the use of comparison flames, produced by the aid of complex mechanism, and a spectro-photometer of original construction. Lithium has been determined more simply, Truchot† having been the first to suggest a method of manipulation which was modified by Ballmann‡ and taken up later by Bell§ apparently without knowledge of the previous work on the same line. Truchot's method consists in comparing the duration and strength of the spectral lines developed by exposure to the Bunsen flame of portions taken up in a platinum loop from the test-solution and standard solutions of different strengths. No analytical proofs of the value of the method were given and accuracy was not claimed beyond the recognition of differences of from three to four milligrams in a liter of liquid when amounts not exceeding forty milligrams per liter were compared. Ballman discards as valueless the observation of the spectral line, advocates the dilution of the test and standard solutions to the absolute extinction of the line, and employs hollow cones, measuring 2.5 mm. by 3.5 mm., to carry the liquids to the flame. Bell follows Ballman's method of diluting the solutions to be compared to a common condition, but takes the vanishing point of the line instead of the point of absolute invisibility and makes his loops of platinum very small. Both Ballman and Bell were able to estimate thallium similarly, but neither determined potassium, Bell declaring specifically that the method is inapplicable to the handling of that element.

Our success in determining potassium qualitatively by the use

*Compt. Rend., lxxvi, 707.
†Compt. Rend., lxxviii, 1022.
‡Zeitschr. für anal. Chem., xiv, 297.
§Am. Chem. Jour., vii, 35.

of powerful flames and coils of large dimensions was such as to encourage the attempt to apply quantitatively the same method of manipulating: and from certain preliminary experiments looking in this direction we found it best, for our purpose at least, to fall back upon Truchot's method of comparing visible lines, rather than to try to fix the vanishing point or the point of extinction of the spectral line. We chose a dilution of the standard solution which corresponds to the presence of $\frac{1}{10}$ mg. of potassium to the coil-full, and set the slit at a width of 0.23 mm., having found it most advantageous to work with lines for comparison bright enough to be visible without much effort. Our mode of proceeding is to dilute the test solution until the line given by the potassium contained in a coil full is of the same brightness as that given by the same quantity of the standard solution. From the final volume of the test solution the quantity of potassium present in it is directly calculable, for, since any given volume of the test solution at its final dilution contains exactly the same amount of potassium as the same volume of the standard solution, we have only to multiply the number expressing the volume in cubic centimeters of the the test solution by the weight in gms. of the potassium contained in one cubic centimeter of the standard in order to obtain the weight in gms. of potassium in the whole test solution. We found it convenient to use several coils adjusted to the same capacity, and to clean, fill, dry, and ignite them before the spectroscope in the manner previously described. From time to time the capacity of the coils should be readjusted, or else the final comparison tests should be made with a single coil. It is essential that the eye of the observer should be kept as nearly as possible in the same condition of sensitiveness and in the same position in making the comparisons, and to accomplish this end we found it best to hold the eye at the observing telescope during the entire intervals between the exposures, to shade it carefully by the hand or otherwise, to cover the eye not in use, to cut off all direct sunlight from the work table, though the diffused light of the room is not objectionable, and to light the comparison slit of the spectroscope to the faintest possible visibility, in order to fix exactly the position in which the line is to be sought. It is important also that the trials of the test and standard should come as closely to

gether as possible in point of time. The observations of a series should be made by the same individual, the preparation and exposure of the wires being made by another. It is not possible to attain the best results in such work single handed. The dilution of the test solution is made conveniently, and with sufficient accuracy, in 100 cc. cylinders graduated to half cubic centimeters, the mixture being made thorough by passing the solutions from vessel to vessel. It is often advantageous to divide a liquid which is to be diluted and to work with aliquot portions, so that it may be possible to retrace a step without trouble in case a portion of the solution has been unwittingly diluted too much; such a mode of proceeding is, of course necessary when the final dilution must exceed 100 cc., unless large graduates are called into use. Excepting the cases of very concentrated solutions, no significant loss of material is occasioned by the filling of the coils, the error thus introduced being trivial in comparison with that inherent in all photometric processes. The following is the record of our experience in the comparison of solutions of pure potassium chloride, the strength of the test solution being unknown to the observer.

Experiment I.		*Experiment II.*	
Volume of Test Solution.	Characteristic of Line Compared with Standard.	Volume of Test Solution.	Characteristic of Line Compared with Standard.
20 cc.	stronger	30 cc.	stronger
50 "	stronger	60 "	stronger
100 "	stronger	82 "	weaker
110 "	stronger	70 "	stronger
120 "	stronger	76 "	stronger
150 "	like	78 "	stronger
200 "	weaker	80 "	like
160 "	weaker		
150 "	like		

(150 × 0.0001 = 0.0150)		(80 × 0.0001 = 0.0080)	
Potassium found	0.0150 gm.	Potassium found	0.0080 gm.
" taken	0.0150 "	" taken	0.0080 "
Limits on either side	0.0120 "	Limits on either side	0.0078 "
	0.0160 "		0.0082 "
Error	0.0000 "	Error	0.0000 "

These results show a degree of accuracy in the process quite unexpected. In the former no attempt was made to approximate as

closely as possible to the limits of dilution on both sides of the condition of equal brightness in test and standard, but in the latter great care was taken in this respect and the possible error cannot exceed two and a half per cent of the entire amount of potassium involved.

Experiment III was made to discover the effect of the presence of a reasonable amount of sodium chloride upon the determination of the potassium. To a portion of the solution of pure potassium chloride containing 0.01 gm. of the element, was added 0.1 gm. of sodium chloride taken from the salt purified as previously described. This solution was diluted and the comparison made with the standard according to the accompanying account.

Experiment III

Volume of the Test Solution	Character of the Light compared with Standard
25 cc.	stronger
50 "	stronger
50 "	stronger
90 "	stronger
95 "	stronger
105	stronger
125	[illegible]

[illegible]

Potassium found	[illegible] gm.
taken	[illegible]
Error	[illegible]

The result of this experiment was most surprising, for instead of diminishing the delicacy of the test we find that the presence of a moderate amount of sodium chloride tends to increase the brilliance of the potassium line. The sodium chloride employed was a part of that prepared and tested as previously described and used in the experiments upon the qualitative determination of potassium. By no possibility could the 0.1 gm. of it taken in the experiment have contained more than [illegible] gm. of potassium. It is evident, therefore, that the brilliance of the potassium line gained twenty per cent in strength by the influence of sodium chloride amounting to ten times the weight of the potassium present when

the effect due to impurity of the salt could by no means exceed a hundreth of one per cent.; that is to say, the observed effect is, at the very least, two thousand times greater than that which might have been conceivably produced by contamination of the sodium salt.

In the following experiment the effect of varying amounts of sodium chloride upon the spectrum of the potassium is shown. The sodium line was turned out of the field of view to obviate the dazzling effect of the sodium light, and a solution of potassium chloride containing 0.01 gm. of the element in 100 cc. was examined spectroscopically after the addition of successively increasing amounts of sodium chloride, the strength of the line observed being brought into comparison with that produced by similar portions of the potassium solution containing no sodium.

Sodium Chloride in a Coil-full.	Potassium in a Coil-full.	Ratio of NaCl : K.	Width of Slit.	Characteristics of Line Compared with Standard Containing no NaCl.
Mg.	Mg.		Mm.	
0.002	0.002	1 : 1	0.18	like
0.010	0.002	5 : 1	0.18	like
0.020	0.002	10 : 1	0.18	a little stronger
0.040	0.002	20 : 1	0.23	much stronger
0.200	0.002	100 : 1	0.23	very much stronger
0.400	0.002	200 : 1	0.23	much stronger
0.600	0.002	300 : 1	0.23	much stronger

From this it appears that the maximum strengthening effect occurs when the sodium chloride stands to the potassium in the ratio of 100 : 1. The apparent diminution of brilliance when the sodium is increased beyond that proportion is doubtless due to the effect of the strong light diffused through the field of view by the intensely bright sodium flame in spite of the fact that the line itself is cut off from direct vision.

The cause of the brightening effect of the sodium chloride we are inclined to attribute to the chemical action of the sodium dissociated in the flame. The effect of ammonium chloride, and of hy-

drochloric acid, in destroying the potassium light is well known and is due, presumably, in very large degree to the prevention of the dissociation of the potassium chloride. The dissociated sodium should naturally by its mass-action reinforce the disintegrating action of the heat upon the molecule of potassium chloride.

It is plain that the complication introduced into the quantitative spectroscopic determination of potassium by the presence of the sodium salt in the test can be obviated if it can be brought about that both the test and the standard solution shall contain the same amount of the reagent. It is a matter of interest, therefore, to discover whether it is possible to match sodium lines of considerable intensity so closely that the quantities of that element in solutions brought into comparison shall be practically equal, and so may be relied upon to give the same strengthening effect to the potassium spectrum. The following statement is the record of an attempt in this direction. The narrower slit was found to be best adopted to the comparison of the sodium lines.

Na Cl in a vol. fol. of New Solution	Na Cl in a vol. fol. of Standard	Width of Slit	Characteristics of lines as compared with that of Standard
Mg	Mg	Mm	
[illegible]	[illegible]	[illegible]	weaker
[illegible]	[illegible]	[illegible]	weaker
[illegible]	[illegible]	[illegible]	weaker
[illegible]	[illegible]	[illegible]	like

The result shows the possibility of matching the sodium lines with a degree of approximation sufficient for the purpose in view and, accordingly, a new standard solution was made containing [illegible] gm. of potassium taken in the form of the chloride and [illegible] gm. of sodium chloride in [illegible] cc. and with this new standard the following determinations were made. The experiment was performed in three stages: first, the test solution was diluted until its potassium line matched approximately with that of the standard; secondly, sodium chloride was added to the solution thus diluted until the sodium lines were brought to equality; and finally, the test solution and the standard were again brought into comparison

Experiment IV.

Part I.			Part II.			Part III.		
Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.	NaCl in 100 cc. of Test Solution.	Width of Slit.	Characteristic of Sodium Line as Compared with Standard.	Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.
cc.	Mm.		Gm.	Mm.		cc.	Mm.	
30	0.23	stronger	0.01	0.18	weaker	108*	0.23	weaker
70	0.23	stronger	0.03	0.18	weaker	108	0.23	stronger
100	0.23	weaker	0.05	0.18	weaker			
			0.08	0.18	weaker	109	0.23	weaker, stronger, like
			0.09	0.18	weaker			
			0.10	0.18	like			

Experiment V.

Part I.			Part II.			Part III.		
Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.	NaCl in 100 cc. of Test Solution.	Width of Slit.	Characteristic of Sodium Line as Compared with Standard.	Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.
cc.	Mm.		Gm.	Mm.		cc.	Mm.	
40	0.23	stronger	0.025	0.18	weaker	160	0.23	stronger
100	0.23	stronger	0.050	0.18	weaker	180	0.23	stronger
160	0.23	weaker	0.085	0.18	weaker	190	0.23	stronger
			0.100	0.18	weaker	200	0.23	stronger
			0.110	0.18	like	205	0.23	weaker
						210	0.23	weaker

$$\left(\begin{matrix} 205 \times 0.0001 = 0.0205 \\ 200 \times 0.0001 = 0.0200 \end{matrix}\right\} \text{ mean} = 0.02025\ )$$

Potassium found . . . . . 0.02025 gm.
" taken . . . . . 0.02000 "
Error . . . . . 0.00025 " = 1.25 per cent.

*Originally present.

(130 × 0.0001 = 0.0130 gm.)

Potassium found . . . . . 0.0130 gm.
" taken . . . . . 0.0140 "
Error . . . . . 0.0010 " = 7 per cent.

Experiment VI.

Part I.			Part II.			Part III.		
Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.	NaCl in 100 cc. of Test Solution.	Width of Slit.	Characteristic of Sodium Line as Compared with Standard.	Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.
cc.	Mm.		Gm.	Mm.		cc.	Mm.	
40	0.23	stronger	0.045*	0.18	weaker	110	0.23	stronger
80	0.23	stronger	0.082	0.18	like	120	0.23	stronger
100	0.23	stronger				130	0.23	like
110	0.23	like						

Experiment VII.

Part I.			Part II.			Part III.		
Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.	NaCl in 100 cc. of Test Solution.	Width of Slit.	Characteristic of Sodium Line as Compared with Standard.	Volume of Test Solution.	Width of Slit.	Characteristic of Potassium Line as Compared with Standard.
						FIRST.		
cc.	Mm.		Gm.	Mm.		cc.	Mm.	
30	0.23	stronger	0.05†	0.18	weaker	100	0.23	stronger
90	0.23	stronger	0.07	0.80	weaker	120	0.23	stronger
100	0.23	weaker like	0.09	8.01	weaker	130	0.23	stronger
			0.10	0.18	like st'nger st'nger	140	0.23	stronger weaker
						SECOND.		
						cc.	Mm.	
						120	0.23	stronger
						140	0.23	stronger
						150	0.23	stronger weaker
						160	0.23	weaker

*The test solution having been acidentally over-diluted, its strength was increased by the addition of 0.0010 gm. of potassium, and this amount was added in the computation below to that originally in the test solution.

(109 × 0.0001 = 0.0109 gm.)

Potassium found	0.0109 gm.	
" taken	0.0110 "	
Error	0.0001 "	= 0.9 per cent.

†Originally present.

	First.	*Second.*
	(140 × 0.0001 = 0.0140)	(150 × 0.0001 = 0.0150)
Potassium found . .	0.0180 gm.	. . . . . 0.0150
" taken . .	0.0150 "	. . . . . 0.0150
Error	0.0010 " = 7 per cent.	. . . . . 0.0000

From these results it is plain that the sodium in test and standard may be matched closely enough to allow a fair approximation to be made in the determination of the potassium. In Experiments IV, V and VI, no readjustment of the percentage of sodium in the final dilution, subsequent to the matching of the sodium lines, was attempted; in Experiment VII this point was looked to, so that in this determination the strength of the sodium was kept equal to that found in the matching process. In experiments IV and VII, the matching of the sodium in the test solution against that in the standard proved to have been exact; in V, an excess of 10 per cent was added, and in VI, the point of equality was thought to have been reached while there was still a deficiency of 25 per cent. in the sodium chloride of the test solution.

The error in the determination of the potassium in Experiment VI may, perhaps, be accounted for by the mistake in matching the sodium; that of the first attempt in Experiment VII, we are disposed to attribute to lack of care in keeping the eye of the observer in the most sensitive condition, and of attention to the point of bringing the wires to the plane in quick succession. The largest absolute error met with amounted to one milligram in a total of fifteen. Though not accurate to the last degree when large amounts of potassium are to be estimated, the method, we think, offers some advantage without too great sacrifice of exactness in the determination of small amounts. In qualitative work the mode of manipulating described is exceedingly satisfactory. Aside from the practical application of the method, the point which has been of greatest interest to us is the development of the fact that the presence of sodium salts in the flame is of direct influence in strengthening the spectrum of potassium.

NOTES.

Labeling Chemical Glassware.—Prof. F. P. Dunnington, in a note under the above caption (JOUR. ANAL. AND APP. CHEM. **5**, 360), recommends grinding a portion of the surface of the glass to prepare it for receiving ordinary pencil marks. I find this unnecessary, and prefer to use the colored pencils especially made for

the purpose by A. W. Faber for writing on glass, porcelain and metal. The small amount of grease in the crayon causes the marks to adhere to the smooth surface of glass, and *grinding* is superfluous. The pencils can be had of all colors. I send with this note a sample pencil to the editor of the JOURNAL OF ANALYTICAL AND APPLIED CHEMISTRY.* H. C. P.

NEW BOOKS.

Hempel's Gas Analysis.† This is in every respect a good book. It is well written, well translated, and well printed. The illustrations, paper and binding are of the best, and the price is moderate. Professor Hempel has confined himself almost entirely to a description of gasometric methods as carried out with the well known apparatus which he devised and perfected. The book is divided into three parts. Part I contains a description of the apparatus and the methods of using it. Part II contains a description of the special methods for determining each gas, and Part III details the practical methods of gas analysis as applied to furnace gases, illuminating gas, etc. The section upon the detection and determination of carbon monoxide is particularly interesting. Prof. Hempel has succeeded in detecting as little as [illegible] per cent carbon monoxide. This was done by [illegible] a mouse between two funnels placed mouth to mouth, drawing [illegible] liters of air through slowly, and examining the blood of the mouse spectroscopically. The author concludes that [illegible] per cent is the smallest amount of carbon monoxide that can be detected with certainty. He considers [illegible] carbon monoxide in the air of rooms prejudicial to health and inadmissible. The translation is a good piece of work. The meaning of each sentence is clear, and the book is written in English. The translator was a student under Hempel and has thus been able to interpret his work better. He has besides made several additions to the text.

Gas analysis has [illegible] very important subject. Hempel's [illegible] by its simplicity and [illegible] ness, and [illegible] work may be done with it is widely used. [illegible] that we now have such an [illegible] it. J. H.

[illegible]

*[illegible] German [illegible] University [illegible]

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PYRITES AS A MATERIAL FOR THE MANUFACTURE OF SULPHURIC ACID

By Wm. H. Adams, M.E.

(Continued from page [illegible])

I have now given, in as concise a manner as possible, all the data necessary to enable the reader to form his own conclusions as to possible supplies of brimstone for the future, costs, etc., and changes or modifications in the methods of securing supplies from this or foreign countries, and also concisely placed before him locations, extent of the deposits, etc., of all the well known pyrites mines, especially so as regards our own country.

There remains the necessity of applying this information to practical uses, and suggesting such advantages as will excite closer investigation, to the end that our own mineral deposits along the entire Appalachian chain may be more fully developed.

There is every incentive to investigate, improve, change and cheapen the methods we are now employing for the utilization of ores containing sulphur, gold, silver, copper, etc.

Owing to the uncertainty of securing supplies of brimstone at any uniform price which will enable manufacturers to calculate as to long time contracts, yet [illegible] the solution of a problem in this regard as the use of [illegible] has already settled so many problems in the old world. [illegible] and manufacture are found wanting [illegible] the United States and Canada. They are [illegible] by the expenditure [illegible] our own people with [illegible] or extraordinary [illegible] people. Let [illegible] be derived [illegible] which can easily [illegible].

The [illegible] new world [illegible] future.

Cost of Sulphuric Acid made from Brimstone.

Four tons brimstone, all costs including freight, losses in transit, burning, etc.; at $24 per ton (product is 18 tons chamber acid daily, or 18 × 322 = 6,000 tons yearly	$ 96.00
Nitrate soda, 6 per cent. of brimstone used, or 538 lbs. daily, at $2.50 per 100 lbs.	13.45
Labor, 5 men, all purposes, at $1.25 per day	6.25
Coal, 2 tons daily, at $3.00 per ton	6.00
Superintendent and office cost	6.00
On works costing $35,000, at 10 per cent. wear and tear,	10.00
Total	$137.70

Or, $7.65 per ton of chamber acid.

Cost of Sulphuric Acid made from Pyrites.

10 tons pyrites, all costs as above, at $5 per ton (product is 18 tons chamber acid, as above)	$ 50.00
Nitrate soda, 4½ per cent. on sulphur contents, or say 400 lbs. at $2.50 per 100 lbs	10.00
Coal, 2 tons daily, at $3 per ton	6.00
Labor, 5 men for all purposes, at $1.25 per day	6.25
Superintendent and office cost	6.00
Wear and tear, as above	10.00
Total	$ 88.25

Or, $4.90 per ton of chamber acid.

This would compare in a business way for a year's working, as follows:

Production of brimstone plant for one year is 6,000 tons chamber acid, at cost of $7.65	$45,900
Production of pyrites plant for one year is 6,000 tons chamber acid, at cost of $4.90	29,400
Yearly difference in favor of pyrites	$16,500

Or about 36 per cent. in favor of pyrites.

Now, if we take the life of a works of this class (in above statement we have charged off ten per cent. yearly for depreciation), the differences in favor of the pyrites plant in ten years would be $165,000. This sum, which is over and above the profits now produced by the use of brimstone, is sufficient to pay for the entire works each three years, or to double the works each two years of working, provided selling prices of the manufactured products were not materially reduced.

The fact should be strongly emphasized that pyrites can be laid down at the average works at prices named above for a term of years.

Also that payments for pyrites belong to and benefit the community we live in, whereas all calculations based upon the use of brimstone from foreign ports are subject to wide fluctuations possible stoppage of supplies in case of war, and payments for the raw product and the freights are paid at all times to foreign owners.

If we take the manufacture of acid phosphates as an example (sulphuric acid being used for no other purpose of consequence in the South) and present a business statement of the costs of same by use of brimstone and of pyrites, it will be found very interesting.

Manufacture of acid phosphate. Works with an output as stated above.

Brimstone Plant in Atlanta, Ga.

[illegible] tons of sulphuric acid [illegible] at $[illegible]	$[illegible]
[illegible] tons phosphate rock [illegible] at $[illegible]	[illegible]
All treatment costs, etc.	[illegible]
	$[illegible]

Product is [illegible] tons, therefore cost of one ton acid phosphate is $[illegible].

Pyrite Plant in Atlanta, Ga.

[illegible] phosphate [illegible] at $[illegible]	$[illegible]
[illegible] phosphate rock [illegible] at $[illegible]	[illegible]
All [illegible]	[illegible]
	$[illegible]

Product [illegible] phosphate is $[illegible].

[illegible] working as follows:

[illegible]	$[illegible]
[illegible]	[illegible]
[illegible]	$[illegible]
[illegible]	$[illegible]

The figures already given as to costs of manufacture of acids and acid phosphates must be sufficiently convincing as to the profitable side of the business, but it requires one or more repetition of the statements made heretofore to illustrate any figures which will bring the benefits of old world working into striking contrast with our own methods of to-day.

Suppose a case where one of the more prominent manufacturers of sulphuric acid, located at present along the seaboard, were educated in the utilization of all the products of such ores as are found in Virginia, North Carolina, South Carolina, Georgia and Alabama, or the same character of ores as are worked in large quantities in European metallurgical establishments.

The location of a works of this class would, of course, be determined by careful study of transportation problems, so that the carriage on raw materials, coal, phosphates, nitrogen compounds, potash, etc., and the transport of the finished fertilizers, acid phosphates, etc., would be favorable in all respects.

The manufacture of the acids in a scheme of this kind would therefore be expressed as follows:

Cost of Sulphuric Acid Produced at the Mine Centers.

10 tons pyrites, all costs of roasting, handling, and preparing for the after treatment of contained metals, at $1 per ton	$ 10.00
Other costs, the same as given in former statement	38.25
Total cost	$ 48.25
Or, on product of 16 tons chamber acid is $3.02 per ton.	

A year's business under such conditions would compare with the present methods as follows:

Production of brimstone plant for one year is 6,000 tons chamber acid, at cost of $7.65	$49,500
Production of pyrites plant at mines, one year, is 5,200 tons chamber acid, at cost of $3.02, say	15,700
Difference is the profit by use of pyrites in the ordinary process of a metallurgical plant	33,800

Taking the utilization of the acid for the manufacture of acid phosphate at the mines and we have the following result:

Cost of Acid Phosphate at Mine Location

5,800 tons sulphuric acid, at $[illegible]	$[illegible]
5,800 tons phosphate rock at $7	[illegible]
All costs of treatment	[illegible]
	$[illegible]

Product is 10,400 tons, therefore, one ton acid phosphate costs $0.68.

It must not be forgotten that the price of acid phosphate only four years ago was about $25 per ton inland, and that during the past ten years it has been possible to manufacture this material, so essential to the welfare of the worn out lands of the South, in Atlanta, and at not to exceed $8 per ton.

It will no doubt surprise many of the manufacturers of acids to learn how general the use of pyrites has become of late years and how widely distributed the operations are, a proof of the gradual and sure education on this subject.

The daily consumption is as follows:

[illegible]	[illegible]
New York and [illegible]	[illegible]
Philadelphia and [illegible]	[illegible]
Baltimore and [illegible]	[illegible]
Southern States	[illegible]
Western States	[illegible]
[illegible]	[illegible]

[illegible]

plants are constantly being erected, but it is not so well known that the older concerns are changing over their plants to the use of pyrites, and that such changes must be more rapid from this time on as competition increases and education in the economical treatment of simple or complex ores becomes more general.

Dr. Francis Wyatt (Eng. and Min. Journal, 1887) says "It is well to remember that we are indebted for the advances in all industrial chemistry, the simplifying of all essential processes which have reduced the cost of bulk chemicals, to so few individuals that they may easily be reckoned upon the fingers of the two hands; and it is a fact illustrative of the obstinancy and conservatism inseparable from ignorance, that those for whose benefit and advantage these labors have been chiefly undertaken, whose vested interests would point them out as most likely to adopt successful improvements on old methods, in order to increase their productions while lessening their costs, have long and sullenly fought, and still continue to fight, on the side of tradition, routine and 'rule of thumb.'"

This ought not to be said of us in this country where every industry is substantially new; where old world prejudices can have obtained no foothold, and where all industrial enterprises are calling only upon trained management of the best class, with education equal to the times in which we live and the competition we are expected to meet.

In closing it must not be expected that very close presentation of details connected with manufacturing will be attempted, these technical matters hardly coming within the scope of so general a presentation of the main features of utilizing pyrites ores; but rather that the statements and tables already given will lead to the further study of subjects useful to each location, and that later references to papers and some of the more promising methods of utilizing the products of pyrites ores may excite such sufficient interest in the possibilities of the establishment of new industrial plants, as will lead to the opening of mines, experimenting, etc., and before long the erection of such combination works as we believe will be generally profitable.

We do not expect that a race of warriors can be husbandmen by fiat, or that husbandmen can become experienced miners, metal workers or chemical manufacturers under the strain of a feverish

and continuous development of natural resources, where the poor of to-day may be, or are expecting to be, the rich of to-morrow. We fully understand that this necessary class of adventurous humanity must be followed by the plodders for subsistence, the men who develop new ideas by slow, laborious methods, and these in turn are followed by a race of men who unite science with ideas already crudely worked out, and eventually the result will be seen by utilization, as before said, of all products under one and the same management.

I have already quoted the great industrial plant at Mansfeld with its colony of [illegible] souls, [illegible] workmen and output of over $7,[illegible] annually. The ores which have supported this immense business for a century, and have been productive for several hundred years, are not valued at over ten dollars per ton as they come from the mine, and the cost of extraction is about seven dollars per ton.

We have ores which could be brought to a common [illegible] metallurgical treatment containing twice as much per ton which [illegible] labor, coal, transport, etc., are not [illegible] what more expensive than in the case of the Mansfeld ores. We have [illegible] products of the ores which would be treated in a centrally located works in the South, [illegible] sulphur [illegible] Mansfeld.

[illegible]

If sulphurous acid is allowed to pass through a hot and not too acid solution of blue vitriol, in such a manner as to keep the liquor in violent ebullition, it will rapidly change the bright blue color of the solution to a dirty green. Addition of water to the green liquid will precipitate copper. Salt will precipitate sub-chloride of copper. These reactions are proof of the reduction of a portion of the sulphate of copper by the sulphurous acid into a sulphate of the sub-oxide, which remains dissolved in the hot solution of blue vitriol. To the presence of the sub-oxide is due the change of color. Now, if air be blown into the dirty green solution, the bright blue color is restored, the re-oxidation of the green sulphate into the blue sulphate. These reductions and oxidations go on indefinitely and practically simultaneously in the apparatus devised by the inventor, Dr. Roessler.

Then we have the Doetsch process, in use on an extensive scale at the Rio Tinto mines in Spain, the essential points of which can be given in a few words. The raw ore, broken to a uniform size of about half an inch, is piled up in heaps from 10 to 13 feet high, channels being left along the bottom and vertical draught holes being provided for. About 2 per cent. of salt is then scattered over the pile, the top of which is about 45 feet wide—a sort of basin being formed 30 feet square—and solutions, obtained after the precipitation of the copper, subsequently saturated with chlorine, are allowed to flow into these basins. The solution acts upon the copper as it trickles downward ; is gathered in gutters, conducted to tanks, made to flow through long sluices, where the copper is precipitated with metallic iron from 110 to 120 parts per 100 parts of precipitate, which averages about 85 per cent. copper.

The solution, after being substantially freed from copper, is dropped through a coke tower, in which it is met by an ascending current of chlorine and hodrochloric acid gas, thus renewing it as a solvent.

For a description of the very perfect method of heap-roasting and lixiviating, practiced at the celebrated Tharsus mines, in Spain, see the article by John Heard, Jr., in Engineering and Mining Journal of August 13, 1887.

In Transylvania considerable pyrites ore containing gold and silver is treated, although many of the mines and works have been

closed within a few years past. The smelting works at Zalathna are using at present a process which has almost wholly superseded all the old methods. The ores which contain free silver and gold amalgamated at the mines, and the tailings, with other ores not put through the mill process, are taken to the smelting works.

These products, averaging 250 to 300 gms. auriferous silver per ton, are calcined either in heaps or in shelf burners. The sulphurous acid which is driven off is utilized for the manufacture of sulphuric acid or other purposes, as will be seen hereafter.

The calcined ores, with a due percentage of raw ores, are smelted in cupola furnaces into regulus, which contains with the precious metals, a little copper and lead; the amount of the gold and silver being from 550 to 650 gms. per ton of regulus, and the copper a little over one half per cent., almost wholly a sulphide of iron.

This regulus is then treated directly with sulphuric acid in lead-lined boxes, after having been ground fine and screened through forty mesh screens. The tanks or boxes have openings for the feeding of the ore and acid, for discharge of the sulphuretted hydrogen gas in manufacture of pure sulphur, and for burning this gas when it is not utilized. The tanks or boxes are heated by steam. 1,000 kilogrammes of regulus are worked in six tanks in twenty-four hours' time, fifteen workmen being required to complete the process. Half the [illegible] by this treatment, the [illegible]

[illegible]

acid to extract the bulk of the copper as sulphate, which is precipitated with iron or crystallized as blue vitriol, while the residues return again to the smelters.

The really interesting portion of the work done is the production of sulphur by the well-known reaction between sulphurous acid and sulphuretted hydrogen. The sulphuretted hydrogen from the treatment of the regulus with sulphurous acid gas from the calcining of the ores, are brought together in wooden towers provided with shelves, over which a solution of calcium chloride trickles to the bottom. If the two gases act upon one another in the presence of water only, the separated sulphur is obtained in a form almost impossible to collect either by filtering or by deposition. The presence of some salt in solution, however, has a very marked and curious action, causing the sulphur to be separated in a form that rapidly and completely settles.

The sulphur so obtained is melted under water at a pressure of 1¾ atmospheres. This process was discovered by Shaffner & Helbig some years ago and published by them, but is practically unknown in this country.

At Meggen, where Germany's large sulphuric acid works are established, a very successful process for the recovery of the residue iron cinder is being worked. It is well known that heating the cinders to expel the last remaining traces of sulphur is very unsatisfactory by reason of the many elements contained in so small quantities; chemical analysis demonstrating the presence of sulphur, iron, selenium, arsenic, lead, mercury, thallium, etc., with zinc sometimes to the extent of 6 per cent.

It is the creation of the sulphates when high heats are used which has long stood in the way of utilization of this residue.

Soaking the refuse in water and thus securing the iron salts is an easy matter, but as the products contain large amounts of sulphate of zinc it is of little practical value, the separation of the two compounds being too expensive. If, however, the liquid in which the refuse has been soaked is treated with an equivalent of common salt for every equivalent of sulphuric acid it contains, the difficulty is overcome. On cooling this liquid, crystals of Glauber's salt are formed, sufficient to pay the expenses of working the residues. The liquid also contains chloride of zinc, besides the sulphates

of iron, zinc and soda. By concentrating the liquid all the salts are separated, leaving pure chloride of zinc in the solution. Thus two valuable products are obtained from treatment of the waste pyrites residues.

At the copper mines in Stadtberg, Germany, worked since [illegible] the ores are carbonates, and sulphides disseminated in slates.

In 1882 experiments were inaugurated looking to treatment of the lower deposits, consisting mostly of sulphurets with cupric chloride, and after some modifications this process is now used generally. Crushers and rolls are used to prepare the ore for the vats and it is then covered for several days with the mother liquor taken from the final process. When thoroughly soaked it is made into piles and exposed to the action of the atmosphere for weeks or months, as the case may be, which exposure converts the sulphide into the soluble chloride, which is extracted with hydrochloric acid.

The copper is precipitated by iron in large agitators. From [illegible] tons of ores are worked by this method annually, and the consumption of iron is almost equal to the copper produced.

Another process somewhat identical with the Stadtberg workings will be interesting to owners of the low grade copper mines of the South, or perhaps not inappropriate as resulting in a process [illegible]

PHOSPHORUS DETERMINATION BY NEUTRALIZATION OF THE YELLOW PRECIPITATE WITH ALKALI

[illegible]

[illegible] accomplished

within 40 minutes, thanks to Dr. Drown, Messrs. Emmerton, Jones, and others, for valuable suggestions regarding the rapid and complete oxidation with permanganate of potash and ultimate reduction of manganese dioxide by tartaric acid now superseded by ferrous sulphate, or, as I prefer, by a few drops of HCl, sufficient only to decompose the manganese dioxide by boiling, the nascent chlorine being also beneficial in hastening oxidation. Much depends upon the preparation of the molybdate reagent. After many experiments I find the following proportions give excellent results:

Take 100 gms. molybdenum trioxide, to which add 150 cc. water, then into it stir well 100 cc. concentrated ammonium hydroxide, then allow the excess of free ammonia to evaporate spontaneously, and lastly pour this solution into 1500 cc. of *cold* dilute nitric acid (1 acid to 2 water).

I have found it very convenient to keep a stock of carefully prepared "yellow precipitate" for standardizing the alkali, which is prepared as follows: Wash the precipitate free from reagents with 3 per cent. nitric acid, then redissolve with ammonium hydroxide (15 per cent.). Remove the filtrate, and boil off nearly the whole of the free ammonia, then add nitric acid (sp. gr. 1.20); precipitate will form immediately; then evaporate to dryness in a porcelain dish, then over the lamp to expel ammonium nitrate and free nitric acid, which may be distinctly observed, resembling the white fumes of sulphuric acid; the point of completion is noted by the fumes ceasing; there is no danger by over-heating during the fuming. Allow to cool off, and keep in a stoppered bottle for standardizing.

Alkali.—Take 6.6 gms. sodium hydroxide, dissolve and dilute with water to 1000 cc.; then 1 cc. corresponds to .0002 phosphorus (approximately), but when standardizing by the "yellow precipitate," the approximation becomes accurate by the addition of a little water.

Acid.—Take 10 cc. nitric acid (1.42), and dilute to 1000 cc. Have ready two burettes graduated in $\frac{1}{10}$ with a capacity of 50 cc., and proceed to make preliminary tests, so that 1 volume acid equals 1 volume alkali, using phenolphthalein as indicator. Start by knowing the acid to be the strongest, then one trial will show their relative values, and a calculation will show the exact amount of water required to reduce the acid to the same strength as the alkali, volume for volume.

Standardizing.—Weigh 0.2 gm. of prepared "yellow precipitate" and run in 20 cc. of alkali, then add the indicator (the size of a pin's head), and stir well till dissolved; now titrate back till one drop destroys the pink, read off, and if it shows 3.7 cc. then the strengths are correct, because 20—3.7 equals 16.3 or .163 per cent phosphorus. Now, supposing the alkali is too strong and therefore shows 15.8 cc., and this divided by 2 = 7.9; so that if 79 cc. are measured off and filled up with water to 815 cc., then the correction will be made exact with alkali. Likewise, take 79 cc. of the acid and fill up with water to 815 cc., then volume equals volume, and 10 cc. equals .10 per cent phosphorus when employing two quantities, say 2 gms. of metal. Several checks may be made in a few minutes, merely for practice with the "yellow precipitate" and afterwards proceed to use the phosphorus taken from samples of metal, etc. The essential point, of course before titration is to have the "yellow precipitate" of constant composition as previously described, and very little practice will enable one to obtain constant results which will not vary more than .005 per cent phosphorus on 2 gms. of steel.

The following details may be resorted to in practice:

For Steel.—Employ 2 gms. dissolve with 50 cc. nitric acid (sp. gr. 1.2) in an Erlenmeyer flask; when the action has ceased (boil on the nitric fumes completely), then oxidize, according to Shimer, with permanganate of potash (1 gm. to the liter). It will be found that 4 cc. is sufficient to form a turbidity which remains permanent for a long time, and this turbidity is the point sought for; which must be redissolved with several drops of hydrochloric acid [illegible] by continuous boiling. When crystal [illegible] fill to mark, off sufficient to [illegible] hydrochloric acid water to [illegible] precipitate slowly [illegible] [illegible] yellow precipitate [illegible] there is a tendency [illegible] greatly vitiate the results [illegible] the presence [illegible] more acid must be added [illegible] but need more

than 3 per cent. excess. Now warm up to somewhere near the boiling point, and add 50 cc. of the molybdate reagent; then immediately shake up the flask for several seconds, and place on a sand bath for 5 minutes, and proceed to filter; wash the filter and the precipitate, with 3 per cent. nitric acid, containing also 3 per cent. potassium nitrate, wash till free from iron and molybdate reagent; finally wash with 3 per cent. nitric acid alone, to remove most of the potassium nitrate. Lastly, dissolve "yellow precipitate" with dilute ammonia (15 per cent.) into a porcelain dish, using a few cc. of hot water for the finish. Now proceed to boil off the excess of free ammonia, then remove from lamp and add 2 cc. nitric acid (sp. gr. 1.20), and the reformation of the "yellow precipitate" will be immediate and complete. Then evaporate to dryness very rapidly, after which raise the heat sufficiently to expel free nitric acid and ammonium nitrate as previously described.

Pig Iron.—Employ varying amounts, according to the grade, that is about 2 gms. for Bessemer and 0.5 gm. for common iron, and dissolve in 1.135 nitric acid, according to Drown. Lastly, proceed, after filtering in the same way as for steel, and oxidize with permanganate, as usual, but be more careful to have the solution after neutralizing perfectly clear with excess of nitric acid.

Ores.—Dissolve 2 to 4 gms. with hydrochloric acid, evaporate to dryness, take up with hydrochloric acid, dilute, and filter, then evaporate to a syrup, and add concentrated nitric acid to decompose the free hydrochloric acid. Lastly, dilute with water, boil and oxidize with plenty of permanganate and proceed as with steel.

The time required for determination of phosphorus in *steel* by the various methods is approximately as follows:

Magnesia method	4 hours.
Emmerton	1½ "
Weighing "yellow precipitate"	2 "
Alkali method	40 minutes.

I do not attempt to make any distinction as to the merit of one method over another, but merely, as Mr. Jones has wisely remarked, on comparative methods, that "the ultimate correction can only result from the product of the experience of many workers," and consequently I shall feel gratified if my attempts at an "incidental improvement" may result in a nearer approach to the standard method.

NOTE ON THE DETERMINATION OF SULPHUR IN SLAGS.

By Joseph Torrey.

In view of Mr. Craig's note in the Journal for January, the following results may be of interest. They were obtained in the winter of 1884, while experimenting on methods of determining sulphur under different circumstances. The method was so nearly identical with that described by Mr. Craig, that I will simply give the results.

Sample.	Percentage of Sulphur.
Black Slag	0.33 0.33 0.35 0.33
Grey Slag	0.92 0.92
"Slag froth"	0.50 0.50
Spiegel Slag	0.61 0.62 0.61

The residue was in all cases tested, but I was unable to find any sulphur therein. The samples were quite different, and varied in age from one to three weeks. Potassium permanganate was used to absorb the evolved hydrogen sulphide.

With regard to the estimation of sulphur in pyrites, I think that in some cases heating the mineral in a stream of oxygen and absorbing the sulphur dioxide in permanganate will give as good results, perhaps, as the method given by Mr. Craig. The residue in the boat should always be thoroughly washed out with hot water, and the filtered wash waters added to the reduced permanganate solution before precipitating with barium chloride. Of course, the object of this note is simply to add a little testimony to the correctness of Mr. Craig's conclusions.

I may add that I think I have seen a note somewhere to the effect that the evolution of hydrogen sulphide in slag sulphur determinations is more complete if magnesium chloride is added with the hydrochloric acid. If I remember correctly, one or two of my analyses were made in this way, but I cannot recall which, and the figures give no evidence.

Chemical Laboratory of Harvard College.
February 6, 1892.

ELECTROLYTIC SEPARATIONS.

By Edgar F. Smith and D. L. Wallace.

In a former communication* from this laboratory, it was shown that gold was completely precipitated from its double cyanide solutions by the current, and further, that it could be deposited equally well from the solution of sodium sulphaurate. When in the latter form, gold can be separated electrolytically from arsenic, tungsten, molybdenum, etc.† During the past year, experiments were instituted for the purpose of ascertaining whether the separation of these metals from gold could be effected as well in the presence of an excess of potassium cyanide. The conditions favorable to these separations are given below.

The temperature appears to exert a marked effect upon the rapidity with which gold is thrown out of solution. In those platinum dishes which happened to be near a window during a cold period, it was noticed that the metal was deposited upon the sides of the dishes farthest from the window; nor was the precipitation in these instances complete. As it seemed to be a matter of interest and importance to know to what extent the deposition of this particular metal was influenced by varying degrees of cold, this subject is receiving special investigation in this laboratory.

GOLD FROM ARSENIC.

Many trials were necessary before the proper conditions for the successful separation of these metals, in cyanide solution, were worked out. Large quantities of alkaline cyanide retard the deposition of the gold, and upon increasing the current in order to precipitate the metal completely, arsenic spots were visible over the entire surface of the gold.

1. To 10 cc. auric chloride (= 0.1240 gm. gold) were added 10 cc. arsenic solution (= 0.1000 gm. of metal), 0.75 gm. of potassium cyanide, and 150 cc. of water. A current generating 1.8 cc. electrolytic gas per minute was allowed to act upon the solution for fourteen hours. The weight of the precipitated gold equaled 0.1248 gm. It contained no arsenic.

*American Chemical Journal 13, 417.
†Proceedings of Chemical Section of Frank. Inst. 3, 20.

2. To 10 cc. auric chloride [illegible] 0.1027 gm. of gold were added 10 cc. arsenic solution [illegible] 0.1000 gm. of metal, 0.75 gm. of potassium cyanide and 150 cc. of water. The current that passed through this solution gave 2 cc. electrolytic gas per minute. The decomposition continued for the same period as in the preceding trial. The gold contained no arsenic, and weighed 0.1027 gm.

3. In this trial, the conditions were precisely like those recorded in 2. The precipitated gold weighed 0.1020 gm.

These results are sufficiently accurate for ordinary analysis. They demonstrate the possibility of the separation in conditions analogous to those above be observed.

GOLD FROM MOLYBDENUM.

This separation gave no trouble. The molybdenum did not show the slightest tendency to separate together with the gold. Stronger currents can be used to advantage in this separation, although those recorded in the following experiments were amply sufficient for the precipitation of the metal in the course of an hour.

1. A current liberating 2 cc. electrolytic gas per minute acted upon the following solution: [illegible] auric chloride [illegible] 0.27 gm. [illegible] ammonium molybdate [illegible] 0.1[illegible] gm. of molybdenum [illegible] gm. of potassium cyanide and [illegible] water. The precipitated gold weighed [illegible] gm.

2. A [illegible] equal to that in [illegible] upon a solution of like constituents, except that the gold [illegible] equaled [illegible] gm. The gold [illegible] weighed [illegible] gm.

3. With [illegible] solution [illegible] weighed [illegible] gm.

[illegible]

[illegible]

then added to the gold double cyanide. Whenever this was done, it was found that the metal separated very slowly when the current acted, and in every case the precipitation was incomplete. To remove this difficulty, the tungstic acid was dissolved in a definite volume of alkaline cyanide, and in this form brought into the gold solution.

1. A current liberating 2 cc. electrolytic gas per minute acted for a period varying from 14 to 16 hours upon the following mixture: 10 cc. auric chloride (=0.1027 gm. of gold), 0.1000 gm. of tungsten, 0.75 gm. of potassium cyanide, and 150 cc. of water. The precipitated gold weighed 0.1020 gm.

2. With a current liberating 2.2 cc. electrolytic gas per minute, and the following: 0.1277 gm. of gold, 0.1200 gm. of tungsten, 0.75 gm. of potassium cyanide, and 150 cc. of water, the deposited gold weighed 0.1285 gm.

3. With conditions similar to those in 2, and a current that liberated 2.4 cc. electrolytic gas per minute, the weight of the precipitated gold equaled 0.1280 gm.

Two trials, in which the acting current gave but 1.6 cc. of electrolytic gas per minute, showed that considerable gold remained unprecipitated. The gold was dark yellow in color. The deposit while rough, without lustre, and for the most part adherent, showed, in spots, a tendency to sponginess.

The experiments recorded above prove that the electrolysis of the cyanide solution may be applied in the separation of gold from arsenic, tungsten, and molybdenum, thus giving a second method for the separation of these metals in the electrolytic way. However, the rapidity with which gold may be deposited from an alkaline sulphide solution, and the wide range of conditions allowed by this solution recommend its use for the separation of gold from the metals under consideration.

GOLD FROM OSMIUM.

In the separations that follow, the osmium was applied as osmiamide. No difficulties were encountered with the conditions as given below.

1. A current liberating 2.4 cc. electrolytic gas per minute, acted for twelve hours upon 0.1277 gm. of gold as chloride, 0.1500 gm.

osmium, 0.75 gm. of potassium cyanide, and 150 cc. of water. The gold deposit weighed 0.1278 gm.

2. A second dish contained 0.1275 gm. of gold, 0.150 gm. of osmium, 0.75 gm. of potassium cyanide, and 150 cc. of water. The solution was subjected to the action of a current giving 2 cc. electrolytic gas per minute. The precipitated gold weighed 0.1275 gm.

3. With conditions the same as in 2, but with a current liberating 2.8 cc. of electrolytic gas per minute, the gold weighed 0.1270 gm.

The deposit of gold in these three experiments was bright and quite adherent.

Cadmium, silver and mercury being metals that are precipitated without special difficulty from solutions of their double cyanides, experiments were made to determine whether their separation from osmium would also be possible. This the results that follow prove conclusively.

CADMIUM FROM OSMIUM

1. A current liberating [illegible] cc. of electrolytic gas per minute acted overnight upon a solution of [illegible] in which were present [illegible] gm. of cadmium, [illegible] gm. of osmium, and [illegible] gm. of potassium cyanide. The deposit of cadmium was all that could be desired. It weighed [illegible] gm.

2. The [illegible] as to the [illegible] the [illegible] cadmium deposit weighed [illegible] gm.

3. [illegible] gas per [illegible]

4. [illegible] weighed [illegible]

[illegible] with all

interruption of the current, if the final traces of metal are desired, and accuracy is sought in the determination.

SILVER FROM OSMIUM.

1. A current, liberating 1.4 cc. electrolytic gas per minute, acted through the night, upon a mixture of 0.1090 gm. of silver, 0.1500 gm. of osmium, 0.75 gm. of potassium cyanide, and 150 cc. of water. The precipitated gold weighed 0.1087 gm.

2. This trial only differed from 1, in having a current of 1.8 cc. electrolytic gas per minute. The weight of silver obtained was 0.1096 gm.

3. In this instance the current was increased to 2.4 cc. electrolytic gas per minute, but the other conditions remained as before. The time required for complete deposition of the silver was seven hours. The deposited silver weighed 0.1088 gm.

MERCURY FROM OSMIUM.

1. 10 cc. mercuric chloride solution (=0.1927 gm. of mercury), 0.1500 gm. of osmium, 1.5 gm. of potassium cyanide, and 150 cc. of water were subjected to the influence of a current of 1.6 cc. of electrolytic gas per minute, for sixteen hours. The mercury deposit weighed 0.1931 gm.

2. 10 cc. mercuric chloride solution (=0.1927 gm. of mercury), 0.1500 gm. of osmium, 1.5 gms. of potassium cyanide, and 150 cc. of water were acted upon by a current generating 0.7 cc. electrolytic gas per minute, for a period of sixteen hours. The precipitated mercury weighed 0.1930 gm.

3. With conditions the same as in 1 and 2, but with a current equal to 1.9 cc. electrolytic gas per minute, the separated mercury weighed 0.1934 gm.

In the separation of gold from tungsten, mention was made of the fact that when the tungstic acid was dissolved in caustic alkali and this solution then added to that of the gold, that the latter metal was incompletely precipitated, although all the other conditions were favorable to its complete deposition. This behavior of the gold led to the introduction of definite amounts of caustic alkali into gold solutions of known strength and containing known

amounts of alkaline cyanide. For example, a current of 1.5 cc. of electrolytic gas per minute, acting upon 0.1277 gm. of gold in the presence of 0.75 gm. of potassium cyanide, precipitated the metal fully in sixteen hours. A similar solution, to which 2 gms. of caustic potash had been added, when acted upon by a current of equal and even greater strength did not yield up any of its metal. Even after longer periods of time not the slightest trace of gold was visible upon the precipitating dishes. Silver, under conditions analogous to those first described for gold, was fully deposited by a current generating 1.4 cc. of electrolytic gas per minute. This is evident from the following trial, which is but one of many that were made.

To 10 cc. silver solution ([illegible] gm. of silver) were added 0.75 gm. of potassium cyanide, 2 gms. of potassium hydroxide and 15 cc. of water. The current employed gave 1.4 cc. of electrolytic gas per minute. The precipitated silver weighed [illegible] gm. Having thus found such a marked difference in the behavior of these two metals under the conditions mentioned, steps were taken to learn what the results would be if both metals were present together. It will suffice to say that their separation [illegible]. Frequently the silver [illegible] was perfectly white in color [illegible] after weighing [illegible] it was discovered to have [illegible]. At times, too, the deposit was [illegible] mixture of the two metals [illegible]

ties of caustic alkali. Repeated experiments were fruitless, and the investigation was accordingly abandoned.

Caustic alkali does not interfere with the electrolytic precipitation of cadmium from solutions of its double cyanide. Reference to the publication of Smith and Frankel* will show that they did not succeed in effecting an electrolytic separation of cadmium from nickel in cyanide solution. It was thought that possibly the introduction of caustic alkali would be efficacious in this instance. The results recorded below prove it to have been of service, and to have made this separation sure and accurate.

1. A current liberating 2.2 cc. electrolytic gas per minute, acted during the night upon 10 cc. cadmium sulphate solution (= 0.1723 gm. of cadmium), 0.1600 gm. of nickel, 2 gms. of caustic potash, 2.5 gms. of potassium cyanide, and 150 cc. of water. The cadmium deposit weighed 0.1723 gm.

2. Conditions as in 1. The current gave 1.4 cc. electrolytic gas per minute. The precipitated cadmium weighed 0.1723 gm.

3. Conditions as in 1; current, however, equal to 2 cc. electrolytic gas per minute. The cadmium weighed 0.1725 gms.

In these and other experiments the deposits were carefully examined for nickel, but it was not found.

Experiments were also made to deposit gold from its solution in ammonium sulphide, but all of the results obtained were low. The separation of gold from tin in solutions of this description also failed. Both metals were present in the metallic deposits. This occurred even on using currents not yielding more than 2 cc. of electrolytic gas per minute.

It is scarcely necessary to mention here, that in all cases in this investigation the metal deposited was examined for that metal with which it had been associated; nor does it appear essential to detail the mode of washing and drying the deposits, as these operations have been fully described in former communications on this subject.

CHEMICAL LABORATORY OF THE UNIV. OF PA.
PHILADELPHIA, February 9, 1892.

*Proceedings Chem. Sec. Franklin Inst. 2, 3.

THE SEPARATION OF IRON, MANGANESE AND CALCIUM BY THE ACETATE AND BROMINE METHODS *

BY R. B. [illegible]

Having in hand the analysis of a series of samples containing iron, manganese and calcium in large amounts it seemed advisable to test the two analytical methods involved namely the separation of iron from manganese by precipitating it as a basic acetate and the separation of manganese from calcium by means of bromine. The object was not so much to test the accuracy of the acetate process as to determine the conditions favorable or otherwise to its successful use. In the case of the manganese calcium separation on the contrary, the value of the method was in question and where either or both constituents are present in quantities its accuracy has been doubted.

For convenience and accuracy standardized solutions of the three substances were used. Piano wire was the basis of the ferric chloride solution. This was dissolved in hydrochloric acid and oxidized by means of nitric acid. The nitric acid was in turn expelled by repeated evaporations with hydrochloric acid. Last traces of ferrous iron were oxidized by bromine. The value of this solution was found by means of a standard permanganate solution.

[illegible]

cipitate was dissolved in hydrochloric acid and the excess of acid expelled by evaporation. This solution was standardized by determining the manganese as pyrophosphate.

	Weight of $MnCl_2$ Solution Taken.	Weight of $Mn_2P_2O_7$ Found.	Weight of MnO in 100 Gms. of Solution.	Mean.
	Gms.	Gms.	Gms.	
(4)	9.98	0.1346	0.6743	0.6739
(5)	10.095	0.1360	0.6735	

The solution of calcium chloride was prepared from calcium carbonate purified by repeated precipitations, as carbonate, by means of ammonium carbonate. It was free from iron, alumina and alkalies.

	Weight of $CaCl_2$ Solution Taken.	Weight of CaO Found.	Weight of CaO in 100 Gms. of Solution.	Mean.
	Gms.	Gms.	Gms.	
(6)	20.094	0.1133	0.5638	0.5633
(7)	20.18	0.1136	0.5632	
(8)	20.19	0.1135	0.5630	

My experiments began with analysis of solutions containing known quantities of the three substances. From this they grew and though the order may be the reverse of a logical one it had best be followed in giving the results.

In the first and second series the quantities of iron and calcium were constant, the manganese was variable. In a third series, containing only manganese and calcium, the proportions of each were varied.

The general mode of operating was the following:

The solutions containing, in the first and second series, the equivalent of about 0.2 gms. of iron and 0.17 gms. of calcium oxide and quantities of manganese oxide varying from 0.03 to 0.2 gms. were diluted to 350–400 cc. To secure the usual conditions of analysis, and because ammonium salts tend to hold manganese in solution, 10 cc. of hydrochloric acid were added. The cold solution was neutralized with ammonia containing ammonium carbon-

ate. The precipitate that might be formed was dissolved with as little as possible hydrochloric acid and 5 gms. of ammonium acetate added.

For the precipitation of the iron and the conversion of the salts of the other elements into acetates this is an unnecessary excess and because of its possible reducing action on the iron salts [illegible] excess should in general be avoided. But preliminary experiments having been made it was believed that with proper [illegible] reduction of the iron might be avoided. To further test this [illegible] ion and because of the influence of ammonium acetate [illegible] manganese salts in solutions this excess was added.

Two acetate precipitations were made. The iron was then [illegible] down a third time with ammonia. In but two cases [illegible] did the third filtrate contain manganese. In making the separation care was taken not to digest the iron precipitate [illegible] vigorously nor too long and as a result there was [illegible] appreciable reduction.

The filtrates from iron, being united, were evaporated [illegible] of ammonia followed by [illegible] water were added to the [illegible] solution which was then [illegible] the water [illegible] until the precipitate gathered [illegible] less [illegible] [illegible]

The [illegible]

The manganese was weighed as pyrophosphate. The iron was determined by the standard solution of permanganate.

The following are the results :

	Weight of Fe Taken.	Weight of Fe Found.	Weight of CaO Taken.	Weight of CaO Found.	Weight of MnO Taken.	Weight of MnO Found.
	Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
(9)	0.2254	0.2251	0.1699	0.1690	0.0341	0.0355
(10)	0.2248	0.2251	0.1700	0.1687	0.0680	0.0689
(11)	0.2252	0.2248	0.1700	0.1696	0.1092	0.1094
(12)	0.2251	0.2251	0.1700	0.1705	0.1500	0.1501
(13)	0.2254	0.2253	0.1702	0.1697	0.2043	0.2053

Error in Weight of	Fe.	CaO.	MnO.
	Gms.	Gms.	Gms.
(9)	0.0003—	0.0009—	0.0014 +
(10)	0.0003+	0.0013—	0.0009 ·
(11)	0.0004—	0.0004—	0.0002 ·
(12)	0.0000	0.0005+	0.0001 +
(13)	0.0001—	0.0005—	0.0010 ·

Experience tells us, that in dealing with such precipitates as those of iron and manganese, repeated precipitation is necessary. In analyzing this necessity and determining its limitations a series of partial separations was made, and the quantities of manganese and calcium in each of the several respective filtrates was determined. The iron, of which about 0.022 gm. was added in each case, was undetermined.

	Weight of Fe Taken.	Weight of MnO Taken.	Weight of MnO Found in First Filtrate From Fe.	Second Filtrate.	Third Filtrate.	Total.	Error.
	Gms.	Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
(14) .	0.2248	0.3341	0.0342	0.0005	none	0.0347	0.0005 ·
(15) .	0.2248	0.0678	0.0681	0.0006	trace	0.0687	0.0006
(16) .	0.2250	0.1088	0.1073	0.0013	none	0.1086	0.0002—
(17) .	0.2252	0.1500	0.1477	0.0024	none	0.1501	0.0001 ·
(18) .	0.2253	0.2042	0.2003	0.0034	trace	0.2037	0.0005—

	Weight of Fe Taken	Weight CaO Found in First Fe Filtrate: First Mn Filtrate	Second Mn Filtrate	Second Fe Filtrate	Total	Error
	Gms	Gms	Gms	Gms	Gms	—
14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
15	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
16	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
18	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

In separating calcium from manganese in the first filtrate from iron three precipitations were made. In no case did the third filtrate contain enough calcium to show.

From the above analyses the necessity of two precipitations in separating manganese from iron and calcium from iron and manganese is evident. More than that seems superfluous.

In general the amount of manganese found in the second filtrate from iron is proportional to its total quantity. It frequently happens, however, that in neutralizing the solution preparatory to the acetate separation the manganese is precipitated and partially oxidized in which case its resolution is impossible. The solution is probably due rather to the action of the air than to any after effect of the acetic acid. In separating manganese and calcium the completeness of a single separation seemed to depend on anything we have noticed from the above analyses as well as on the nature of the precipitate separated as well as its quantity.

It will be [illegible] exception [illegible] with the exception [illegible] The [illegible] The precipitate in the case [illegible] precipitate. The [illegible] weight of the [illegible]

The [illegible] necessary where [illegible] quantities [illegible] cents [illegible] weight [illegible]

proximately kept, 5 gms. of ammonium chloride and 10 gms. of ammonium acetate were added in each case. Only the calcium of the first manganese filtrate was determined.

	Weight of MnO Taken.	Weight of CaO Taken.	Weight of CaO Found in First Filtrate.	Loss.
	Gms.	Gms.	Gms.	Gms.
(19)	0.2042	0.1702	0.1639	0.0063
(20)	0.1020	0.1705	0.1638	0.0077
(21)	0.0508	0.1702	0.1662	0.0042
(22)	0.0207	0.1702	0.1682	0.0018
(23)	0.2039	0.0848	0.0779	0.0069
(24)	0.1020	0.0849	0.0831	0.0018
(25)	0.0516	0.0855	lost	. . . .
(26)	0.0204	0.0846	0.0833	0.0013
(27)	0.2037	0.0423	0.0399	0.0024
(28)	0.1023	0.0427	0.0421	0.0006
(29)	0.0512	0.0424	0.0415	0.0009
(30)	0.0203	0.0428	0.0421	0.0007
(31)	0.2037	0.0171	0.0141	0.0030
(32)	0.1023	0.0173	0.0158	0.0015
(33)	0.0509	0.0170	0.0167	0.0003
(34)	0.0207	0.0171	0.0162	0.0009

These results indicate that the amount of calcium, carried down with the manganese, depends largely on the relative quantities of manganese and calcium. However this may be, it is evident that where the amounts of each are not less than 0.02 gm. a double precipitation of manganese should be made.

Having introduced such large quantities of ammonium salts into the solutions, the question of effect on the oxalate precipitate was raised. Attention has been called to the negative calcium error. Is this due simply to the solubility of the oxalate or is it the sum of large positive* and larger negative errors?

In answer to this suggestion a number of calcium determinations were made, in which the previous conditions, as to quantity of ammonium salts and volume of solution, were observed.

*The source of positive error would be the reagents and glassware. The operations, excepting the precipitation of manganese by bromine, were carried on in platinum. The ammonium hydrate and sulphurous acid were freshly prepared. The other reagents were carefully tested

	Weight of CaO Taken.	Weight of CaO Found.	Error.
	Gms.	Gms.	Gms.
(35)	0.1136	0.1131	0.0005—
(36)	0.1138	0.1135	0.0003—
(37)	0.1136	0.1136	0.0000
(38)	0.1139	0.1137	0.0002—
(39)	0.1136	0.1132	0.0004—
(40)	0.1138	0.1133	0.0005—

The solution 300 cc. contained approximately 5 gms. of the chloride, 5 gms. of the acetate and 10 gms. of the bromide of ammonium. The inference is that their influence in restraining the oxalate precipitation is slight.

Summary: In precipitating iron as basic acetate it is probably better to avoid a great excess of the acetate. A considerable excess need not, however, interfere with the separation. While an acetate solution favors the reduction of iron, with care this reduction may be avoided. The precipitate should not be digested too vigorously nor too long.

In neutralizing the solution, preparatory to the acetate separation, a slight precipitate of manganese, due to oxidation, is almost always formed. This influences more or less markedly the completeness of a single separation. It cannot be wholly avoided, though the effect of the presence of ammonium salts, in holding manganese salts in solution, is probably beneficial. While the manganese remains in solution oxidation cannot take place.

In precipitating manganese from an ammoniacal solution by means of bromine the presence of acetates is desirable. The oxidation is more rapid, hence more complete than in a solution free from acetates. Bromine water should be added to the hot ammoniacal solution. If the solution be cold the oxidation is slow and in the end often incomplete. The addition of bromine to the solution already made ammoniacal seems preferable to a reversal of this order as it insures a more uniform oxidation.

Where either the calcium or the manganese is in excess of 0.02 gms. two precipitations are necessary.

In conclusion it may be said that, in the hand of a careful analyst, both methods are, according to present standards accurate.

CHEMICAL LABORATORY, TRINITY COLLEGE,
HARTFORD, November, 1891.

INVESTIGATION OF MILK TESTS.*

COMPARISON OF BABCOCK TEST WITH THE CHURN AT THE AMERICAN DAIRY SHOW AND AT THE STATION.

By E. H. Farrington.

The milk given at one milking at 2.30 p. m., November 18th, by the two Brown Swiss cows tested at the dairy show at Chicago, was taken for churning. The milk weighed 52 lbs., and by test contained 1.971 lb. butter fat. It was run through a "Baby" hand separator No. 2. Several samples of the skim-milk were taken as it came from the separator, which showed only a trace of butter fat. The cream weighed 10.25 lbs., or 19.7 per cent. of the new milk. The tests showed that the cream contained 19.23 per cent. butter-fat. This cream was ripened for about 24 hours and then churned. The details of the results are given in the table below.

During the progress of the Dairy Show a working dairy was in operation. For this thirty cans of milk were received. Wednesday, Nov. 18, this milk weighed 2,035.25 lbs. It was put in a large vat, warmed, and thoroughly mixed. The thoroughness of the mixing is illustrated by the fact that tests of four samples showed no variation in the per cent. of butter-fat. One sample was taken from the middle of the vat, two from the ends, and one from the first milk drawn from the faucet. The milk contained 4.15 per cent. of butter-fat, or 84.45 lbs. in the 2,035.25 lbs. milk.

This milk was run through a separator in 65 minutes. The speed of the separator was said to be 6,000 revolutions per minute. Traces only of butter-fat were found in four samples of the skim-milk taken during the process of separation. It required 9.8 cc. of one-tenth normal alkali to make 50 cc. of the milk neutral. After ripening for 24 hours the cream was churned. Details are given in the table above.

The butter obtained from the 52 lbs. of Brown Swiss milk was about 3 oz. more than the butter-fat in the same milk, as indicated by the tests of the new milk. The butter obtained from the 2,035.25 lbs. of milk used in the working dairy was 20 lbs. more than the butter fat shown by tests of the milk. This is an increase of the churn over the test of 11.5 and 23.6 per cent. respectively.

*Bulletin Agrl. Expt. Station, Champaign, Ill., Nov., 1891.

Results Obtained from the Churnings.

	Cream from Milk of	
	Brown Swiss Cows.	Working Dairy.
Weight of cream churned	10.25	. . . .
Temperature of cream churned	61° F.	61° F.
Temperature of buttermilk	59° F.	61° F.
Time of churning	65 min.	17 min.
Acidity of cream [50 cc. 1-10 normal alkali]	25.5 cc.	37 cc.
Weight of buttermilk, lb.	15	204.5
Per cent. of fat in buttermilk	0.6	0.3
Weight of salted butter from churn, lb.	2.1875	104.5
Weight of butter-fat by test of milk, lb.	1.971	84.46
Difference	0.2165	20.04
Percentage increase of churn over test, or of butter over butter-fat in the milk	11.5	23.6
Analysis of butter—		
Water, per cent.	15.4	14.15
Butter-fat, per cent.	77.24	82.
Salt, per cent.	6.6	3.
Curd, per cent.	0.76	0.85
Total	100.00	100.00
Pounds of butter-fat in the butter	1.689	85.69
Pounds of butter-fat in the buttermilk	0.09	0.61
Total	1.779	86.30
Pounds of butter-fat in the milk used, as shown by test	1.971	84.46
Difference—loss or gain in the process	—0.192	+1.84
Per cent. which loss or gain was of total butter-fat in milk used	—9.7	+2.17

From analyses of the butters, with the records of weights of butter and butter-milk, the account kept with the Brown Swiss milk shows a loss of 0.19 lb. butter fat, or 9.7 per cent. of the total weight of butter-fat in the milk started with. Although this is not the finest working that can be done, so small a quantity could easily be lost by adhering to the dairy utensils of processes through which the milk passes to make butter. The account kept with the 2,035.25 lbs. of milk in the working dairy shows an increase of 1.84 lb. of butter fat over the total quantity in the fresh milk as

tested. This figurative creation of butter-fat in excess of what there was in the milk is probably due to the water that the 13 wooden boxes absorbed after they were weighed. The helper who packed the butter into boxes from the churn had weighed the dry boxes, then dipped each one into cold water, filled it with butter, and from the total weight subtracted the weight of the dry box, so that the water absorbed by the boxes appears as weight of butter.

The salt added to the butter from the Brown Swiss milk was not weighed, but estimated by the helper, and the analysis of the butter shows an excessive quantity.

A comparison of the test and the churn has been made at the dairy of this Station, together with an analysis of the butter, and the accounts balanced well. This work, except the last two churnings, was done by one person, and the dairy utensils used were carefully cleaned to prevent any loss of butter-fat in the process. The milk used was from one Jersey cow about one month after calving. In four trials the milk was set in Cooley cans with bottom faucet. Another trial (the third in the tables) was made by setting the milk in shallow pans, which were the common kind used for this purpose, but with a hole at one side near the bottom. This hole was closed with a cork until time to skim the milk, when, by pulling the cork, the skim-milk was drawn off till the cream fell to the hole and then the cork was replaced.

The results from the five churnings (next page) illustrate a gradual change from a loss to a profit by attention to the proper temperature and acidity of the cream churned. In the first trial the temperature of the cream was too high and the cream was not sour enough. This caused a loss of 5.3 per cent. of butter-fat in the buttermilk; and the butter obtained was 10 per cent. less than the total quantity of butter-fat in the milk used.

A test of the buttermilk is a good guide for judging of the thoroughness of the churning, and in the above record it can be seen that the per cent. of butter fat in the butter-milk gradually decreases from the first to the fifth trial, in which the cream was churned in about proper condition as to temperature and acidity, giving a butter-milk which contained only 0.1 per cent. butter-fat and a weight of butter 16 per cent. greater than the butter-fat in the original milk. The butter was weighed and a portion taken

Record of the Weights and Tests of the Whole Milk and Skim Milk

Date	Whole Milk			Milk set in [illegible]	Skim Milk		
	Pounds	Per cent	Pounds		Pounds	Per cent	[illegible]
First Trial							
Oct. 16 a. m.	12.18	[illegible]	[illegible]	24 hours	[illegible]	[illegible]	[illegible]
Oct. 16 p. m.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Oct. 17 a. m.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Oct. 16 a. m.	[illegible]	[illegible]	[illegible]	24	[illegible]	[illegible]	[illegible]
Total			[illegible]				[illegible]
Second Trial							
Oct. 16 p. m.	[illegible]	[illegible]	[illegible]	[illegible] hours	[illegible]	[illegible]	[illegible]
Oct. [illegible] a. m.	[illegible]	[illegible]	[illegible]	24	[illegible]	[illegible]	[illegible]
Oct. [illegible] p. m.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Oct. [illegible] a. m.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Total			[illegible]				[illegible]
Third Trial. Milk [illegible] Five Minutes [illegible]							
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]			[illegible]				[illegible]
[illegible]							
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]			[illegible]				[illegible]
[illegible]							[illegible]
[illegible]							[illegible]
[illegible]							[illegible]
[illegible]							[illegible]
[illegible]							[illegible]

Results Obtained from the Churnings.

	First Trial.	Second Trial.	Third Trial.	Fourth Trial.	Fifth Trial.
Temperature of cream churned, F.	68°	80°	66°	62°	58°
Temperature of buttermilk, F.	64	74	62	60	58
Time of churning, minutes	15	3	10	7	20
Acidity of buttermilk [50 cc. = 1-10 normal alkali]	13 cc.	35.5 cc.	28.5 cc.	36.5 cc.	41.6 cc.
Weight of buttermilk, lb.	8	8.56	3.875	6	6.78
Per cent. of fat in buttermilk	5.3	4.9	1.25	0.35	0.1
Wt. of unsalted butter from churn	1.75	2.34	1.8125	1.84	2.156
Wt. of butter-fat by test of milk	1.955	2.365	1.6006	1.619	1.848
Differ'e—loss or gain in the process	—0.205	—0.025	+0.2119	+0.221	+0.308
Per cent. which loss or gain was of total butter-fat in milk used	**—10.4**	**—1.06**	**+13.24**	**+13.64**	**+16.65**
Analysis of butter—					
Water, per cent.	19.56	21.33	15.66	14.95	15
Butter-fat, per cent.	78.94	77.	82.54	83.27	83.2
Curd, per cent.	1.5	1.67	1.8	1.78	1.8
Total	100.00	100.00	100.00	100.00	100.00
Pounds of butter-fat in the butter	1.381	1.8018	1.496	1.535	1.7939
Pounds of butter-fat in the buttermilk	0.424	0.4194	0.0484	0.021	0.0067
Pounds of butter-fat in skim-milk	0.141	0.1256	0.0547	0.083	0.0847
Total	1.946	2.3470	1.5991	1.639	1.8853
Pounds of butter-fat in the milk used, as shown by test	1.955	2.365	1.6006	1.619	1.848
Differ'e—loss or gain in the process	—0.009	—0.018	—0.0015	+0.02	+0.037
Per cent. which loss or gain was of total butter-fat in milk used	**—0.46**	**—0.7**	**—0.1**	**+1.23**	**+2.**

for analysis before it had been worked. This accounts for the large per cent. of curd found by the analysis. The cream used in these five churnings was separated from the milk in different ways. All the milk was set at a temperature of 45° to 48° F., either in Cooley cans with bottom faucets, or in shallow pans. The cream was not skimmed from the milk in the shallow pans, but the skim-milk was drawn off at the bottom of the can as before described.

This figure illustrates a device for measuring the acid used with the Babcock milk test. By this arrangement the glass automatic

pipette can be put through the cork of any bottle of acid, which is also kept closed, thus preventing any change in the strength of the acid.

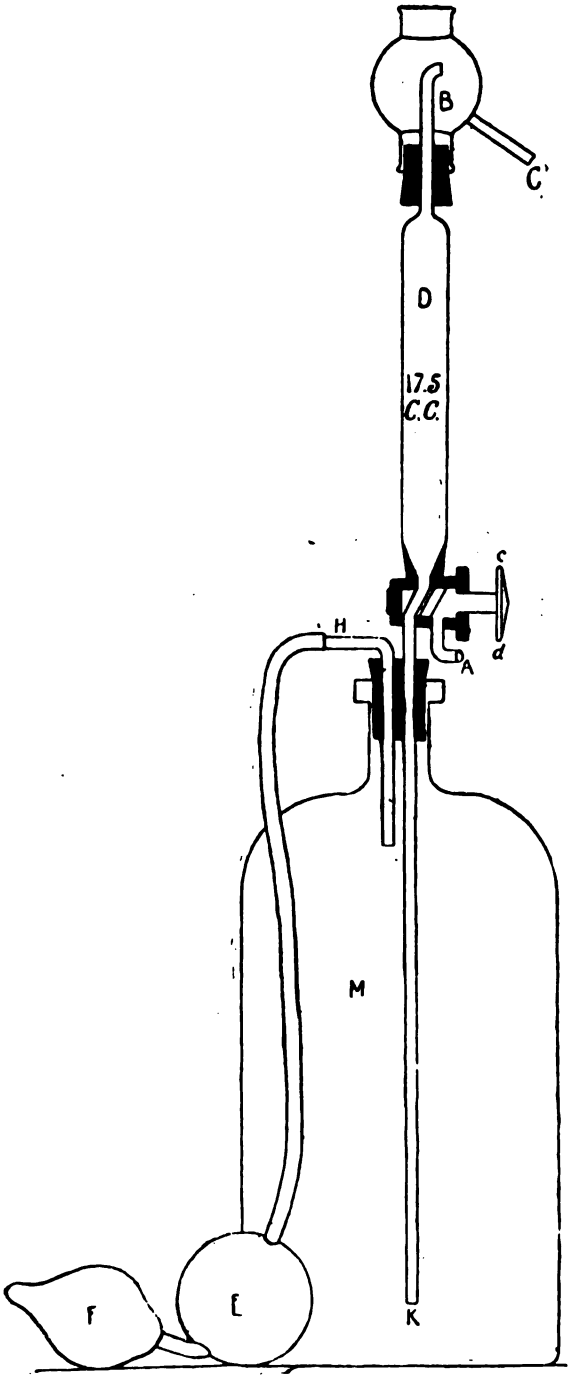
A system of valves is so arranged in the rubber bulbs *E*, *F*, that by squeezing *F* in the hand air is forced through the tube *H* into the bottle of acid *M*. This pressure of air forces the acid through the tube *K* up into the pipette *D* until it overflows at *B*; then by turning the cock so that *c* and *d* change places the connection is closed between the bottle and pipette and opened from the pipette out through the tube *A* from which the measured acid is delivered into the test bottle.

The end of the tube *H* inside the bottle should not touch the acid, but the end of the tube *K* should always be in it. This tube *K* should be of stout glass with an inside diameter of 3-16 in., the holes through the glass cock should be 1/8 in., and the delivery tube *A*, from the pipette to the test bottle, should have an inside diameter of 1/8 in. and an outside diameter of 7-32 in.

MARKING TEST BOTTLES.

The common practice now is to mark milk test bottles with a numbered ring or band of copper around the neck of the bottles. In keeping up the supply of test bottles it often happens that new ones have the same numbers as those already in use. Two bottles with the same number may cause confusion and guess work, if two different samples of milk are tested in them at the same time. The enlarged end of the neck of the test bottle often breaks off and though the break may not be sufficient to prevent using the bottle, the copper band easily slips off and is lost.

A simple and efficient way of marking test bottles is to grind a label on them with a file. Wet with water a flat side of a three-cornered file and use the wet side of the file. File a space about one-fourth inch square at any convenient place on the test bottle, thus making the smooth surface of the glass rough and on this ground label mark numbers with a lead pencil. A good place to file the label is either above or below the graduation on the neck of the test bottle.


B
C
D
17.5
C.C.
c
d
A
H
M
E
F
K

COMPOSITE MILK SAMPLES TESTED FOR BUTTER FAT

A report was made in bulletin No. [illegible] of this Station of trials at the creameries of H. B. Gurler, DeKalb, and at the Station [illegible] a method of using composite samples in testing milk. The method of collecting the samples was first described by Professor Patrick in bulletin No. [illegible] of the Iowa Station. The formula tested in the trials made at DeKalb had been sent by Professor Patrick to Mr. Gurler at his request. As pointed out by Professor Patrick, an objection to his method is that the preservative used is a [illegible] poison. To avoid this objection a comparison was made of this method with one suggested by the writer in which the milk was not preserved but collected for a week and allowed to sour. By adding to a pint of the sour milk about one half a teaspoonful of powdered lye and mixing carefully it was demonstrated that composite samples of milk could be accurately tested for fat without the use of corrosive substances.

This use of powdered lye has proved very practical [illegible] in [illegible] during the past seven years and is now [illegible] by them. It [illegible] milk [illegible] [illegible] Although [illegible] [illegible] [illegible]

[illegible]

Butter-Fat Shown by Weekly Composite Tests, Per Cents.

No. of Patron.	Week Ending October				
	2nd	9th	17th	24th	30th
1	4.3	4	4	4.4	4.2
2	3.6	3.3	3.6	3.7	3.5
3	3.6	3.5	3.6	3.7	3.7
4	3.6	3.5	4	4	4.2
5	3.8	3.6	3.6	3.6	3.6
6	3.9	3.6	4	4.1	3.9
7	3.8	3.8	3.8	3.4	3.6
8	4.4	4.8	4.4	4	3.9
9	3.5	3.6	3.4	3.8	out
10	4	4.3	3.8	4	4.4
11	3.9	3.7	3.7	4.4	3.2
12	3.6	3.7	3.7	3.4	3.4
13	3.9	3.7	3.7	4	3.8
14	4	3.9	3.9	4	4.1
15	3.7	3.8	3.8	4	4.1
16	4	3.6	3.6	4	4.1
17	3.6	3.6	3.6	3.6	3.7
18	3.6	4	4	3.8	3.6
19	4.2	4.6	4.6	4	4.2
20	3.6	3.6	3.6	4	3.8

"Some of the variations I can account for. No. 11, for instance, had a steady increase in milk from fresh heifers. Some had a decrease from their cows drying off. In the summer months when the conditions of the different dairies were more uniform, the tests ran with a surprising uniformity."

CREAM SEPARATION, TEST OF METHODS.

A number of trials were made to observe the completeness of the cream separation after the milk had been set in Cooley cans, temperature 45° to 48° F., 12, 24, 36, and 48 hours. Tests for butter-fat were also made of the skim-milk in the bottom and the middle of the can, and of that last drawn off.

The results show that cream is often lost if the skim-milk is drawn off nearer than one inch from the bottom of the cream. The variation in the tests given in the table on p. 29 under the column headed "last skim-milk" shows the necessity of caution in skimming close to the cream. Drawing off the skim-milk to within one inch of the bottom of cream can be done without loss of cream, if the faucet is set so that the skim-milk does not stop

running until it has reached the point where you wish it to stop; repeated opening and closing of the faucet has a tendency to mix the cream so that it flows out with the skim-milk.

The summary of this table shows that when the milk of this cow was set in cans to the depth of ten inches the most butter-fat was obtained in the cream when the milk had been set 48 hours.

Records of the Weights and Tests of the Whole Milk and Skim-Milk.

Date.	New Milk Set. lb.	Milk Used.	Per Cent. Butter-Fat in Skim-Milk Drawn. Bottom	Middle	Last	Total	Per Cent. of Total Butter Fat of New Milk Left in Skim-Milk.	
Milk skimmed after standing 12 hours—								
Oct. 16	10.18	5.8	0.6	0.8	2	1.2	15.76	Average 12.87
Nov. 1	7.5	5	0.4	0.6	0.7	0.7	10.55	
Nov. 4	7.93	5.7	0.5	0.8	3.9	1	12.3	
Nov. 5	*8.5	4.6	0.1	0.2	1.9	0.4	*7.34	5.18
Nov. 6	*8.56	5.2	0.2	0.3	0.5	0.2	*3.03	
Milk skimmed after standing 24 hours—								
Oct. 16	12.22	3.9	0	0	0.5	0.2	3.9	3.7
Oct. 19	11.43	3.6	0	0.1	1.9	0.2	4.38	
Oct. 20	12	5.3	0	0.3	0.7	0.4	5.34	
Nov. 1	9.68	3.9	0.2	0.3	0.3	0.2	4.1	
Nov. 2	10.37	5.2	0	0	2.2	0.2	2.87	
Nov. 3	9.87	4.0	0	0	0.4	0.1	1.6	
Nov. 5	*9.75	3.7	0	0	1.4	0.05	*1.17	1.62
Nov. 6	*9.84	4.1	0	0.2	0.4	0.1	*2.06	
Milk skimmed after standing 36 hours—								
Oct. 19	10.5	5.8	0	0.2	6.6	0.4	5.37	4.05
Oct. 31	10.18	4	0	0.1	0.8	0.2	3.9	
Nov. 2	8.93	5	0	0.1	2.1	0.2	2.88	
Milk skimmed after standing 48 hours—								
Oct. 17	11.68	4.1	0	0	0.4	0.1	2	2.4
Oct. 21	12.59	4.7	0	0	1.8	0.2	3.4	
Nov. 4	11.25	4.4	0	0.1	1.6	0.1	1.81	
Milk diluted with an equal weight of water and skimmed after standing 2 hours—								
Nov. 7	9.62	4.9	0.4	0.5	0.5	0.5	17.2	

*Shallow pan, milk 3 inches deep.

This was not much better than setting the milk 24 hours, but considerably better than setting 12 hours. An average of 2.4 per cent. of the total butter-fat in the new milk was lost in the skim-milk when skimmed after 48 hours standing; 4.05 per cent. after 36 hours; 3.7, after 24 hours; and 12.87, after 12 hours.

Summary.—Per Cent. of the Total Butter-Fat in the Milk Left in the Skim-Milk.

	Milk Set in Cans. Depth of Milk, 10 Inches.				Milk Set in Shallow Pans.		Diluted with One-half Water.
Time of setting, h.	12	24	36	48	12	24	2
Per cent. of total .	12.87	3.7	4.05	2.4	5.18	1.62	17.2

Milk Set in Shallow Pans 3 Inches Deep and in Bottles 6 and 9 Inches Deep.

No. of Trial.	Manner of Setting.	Temp. F. of Milk when Set.	After 1 Hour.	After 2 Hours.	Milk Used.	Per Cent. of Butter Fat in Skim-Milk After Standing. 1 Hour.	2 Hours.	3 Hours.	6 Hours.	9 Hours.	24 Hours.
1	Shallow pan, depth 3 inches	95°	82°	77°	3.3	. .	1.9	1.5	0.8	0.6	0.1
	Bottle, depth 6 inches	95	. .	. .	3.3	2.9	2.3	2.1	1.4	0.9	. .
	Shallow pan, half water, 3 inches	73	71	70	3.3	. .	0.4	0.25	0.1	0.05	. .
2	Shallow pan, depth 3 inches	97	85	79	2.9	2.5	2	1.6	1	0.6	0.15
	Bottle, depth 9 inches	97	. .	. .	2.9	2.7	2.3	2	1.5	1.2	0.5
	Pan, half water, 3 in.	75	72	72	2.9	0.6	0.4	0.3	0.15	0.05	. .
3	Shallow pan, depth 3 inches	96	85	82	3.45	2.4	2	1.6	1	0.7	0.4
	Bottle, depth 9 inches	96	86	82	3.45	2.8	2.4	2.2	1.6	1.2	0.9
	Pan, half water, 3 in.	76	74	74	3.45	0.5	0.4	0.3	0.1	0.05	. .

One trial of separating the cream by diluting the milk with an equal volume of water, showed that 17.2 per cent. of the total butter-fat was lost in the skim-milk when skimmed after 2 hours standing. The results obtained from setting the milk in shallow pans showed the most complete separation of cream in this trial. Only 1.62 per cent. of the total butter-fat of the milk was lost

in the skim-milk after standing 24 hours, and 5.18 per cent. after standing 12 hours.

More uniformly complete separations of cream than any of the above can be obtained by using a "Baby" hand separator, which we have repeatedly tested, obtaining skim milk with less than .1 per cent. butter-fat.

Equal Parts New Milk and Water

			Temperature							Per cent. Butter-fat				
			Initial	Milk	Water	Initial Milk	Water	Initial		Milk	Initial	Skim	Milk	Water
Cow No. 1	July	1	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]			[illegible]
		2	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]			[illegible]
		3	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]			[illegible]
		4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]		[illegible]
Cow No. 2	July	1	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]			[illegible]
		2	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]			[illegible]
		3	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]			[illegible]
Cow No. 3	July	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]		[illegible]	[illegible]	[illegible]		[illegible]
		3		[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]		[illegible]
Cow No. 4	July	1	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]			[illegible]		[illegible]	[illegible]
		2		[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]			[illegible]
		3		[illegible]	[illegible]	[illegible]		[illegible]		[illegible]	[illegible]			[illegible]
		4	[illegible]	[illegible]	[illegible]					[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]					[illegible]				
				[illegible]										
Cow No. [illegible]			[illegible]		[illegible]	[illegible]		[illegible]			[illegible]			[illegible]
					[illegible]	[illegible]		[illegible]		[illegible]				[illegible]
					[illegible]			[illegible]						[illegible]
Mixed Milk [illegible]			[illegible]	[illegible]	[illegible]	[illegible]		[illegible]						[illegible]
[illegible]					[illegible]					[illegible]	[illegible]			[illegible]
								[illegible]		[illegible]				[illegible]
Mixed Milk [illegible]								[illegible]			[illegible]	[illegible]	[illegible]	[illegible]
[illegible]												[illegible]		[illegible]
										[illegible]		[illegible]		[illegible]

[illegible] the rate at which [illegible] and [illegible]

deep. A mixture of milk from several cows was used and it was set in a room where the temperature was about 70° F. In each trial the cream rose faster and more completely in the shallow pans 3 in. deep than when set in bottles 6 or 9 in. deep. See foregoing table for results.

CREAM RAISING BY DILUTION.

The observations here recorded include a comparison of the rate at which cream rises in hot weather, when the milk of different cows is diluted with an equal volume of water. The benefits of this practice are supposed to be obtained by dairies which do not have ice or a cool place in which to set milk, and where in hot, muggy weather the milk sours before all the cream rises. Under such circumstances it has been suggested that the cream can be separated at once, by adding cold water to the new milk.

The following trials were made to demonstrate how thoroughly the cream can be separated in this way, and what results would be obtained with the milk of different cows. About one-half a pint of new milk was mixed with the same quantity of water. The mixture was put into wide mouthed glass bottles with a faucet at the bottom by which portions of skim-milk were drawn off for testing. The mixture filled the bottles to a depth of 4 in. The temperature of the milk was about 98° F. when mixed with water of about 58° F. The temperature of the mixture was about 75° F., and it was kept in a room where the temperature ranged from 66° to 76° F. A test was made of the skim-milk after the mixture had stood 1, 2, 6, and 9 hours.

The details are given in the foregoing table:

The milk used, 250 cc., was carefully measured each time. A calculation has been made to show the per cent. of the total butter fat of the milk which was left in the skim-milk.

Percentage of Total Butter-Fat Left in the Skim-Milk.

Milk Set.	1 Hour.	2 Hours.	6 Hours.	9 Hours.
Cow No. 1, av. of 6 trials	46	35.5	22.4	14.9
" 3, " 3 "	35.5	28.7	14.7	10.4
" 4, " 6 "	50	33	16.8	17.3
" 5, " 3 "	43	. . .	. . .	15.8
Mixture, 1, " 3 "	31.5	. . .	. . .	15
" 2, " 3 "	34.7	23.3	13.9	10.4
Average	40.1	30.1	17	14

These tables show that there was quite a variation in the per cent. of butter-fat found in the diluted skim milk from the milk of the same cow on different days. These variations were not so great, however, as that of cow No. 1 from all the others. The milk from cow No. 1 was considerably richer than that from the others and gave a richer skim milk, but it contained about the same proportion of the total butter fat as the milk from the other cows.

The average of all the results obtained shows that in this trial when new milk was diluted with an equal volume of cold water and kept in a room at about 75° F., there was left in the skim milk about 40 per cent. of the total butter fat after standing one hour, 30 per cent. after two hours, 17 per cent. after six hours, and 14 per cent. after nine hours.

An experiment was next made to ascertain whether the quick raising of cream by dilution was caused by the sudden change in temperature or by the dilution of the liquid through which the fat globules rise.

Milk Skim Kept [illegible] Hours.

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

The bottles used before were filled to the same depth with new milk. They were then put into a refrigerator until the milk had cooled to about 75° F., taken out and kept in a room at 70° to 75° F.

The details of the record are given in the table.

An average of the duplicate trials shows a great difference in the cream rising on milk of the different cows. There is not near the uniformity that was observed when the milk was diluted with water.

The same calculation used before shows the per cent. of the total butter-fat of the whole milk left in the skim-milk to be as follows:

Per Cent. of the Total Butter-Fat left in the Skim-Milk.

Milk Set.	1 Hour.	2 Hours.	6 Hours.	9 Hours.
Cow No. 1.—July 16	30.6	24	12	9.3
" 17	25.1	14	9	3.4
Average	26.8	19	10.5	6.3
Cow No. 3.—July 16	73.5	60.3	33.5	13
" 17	60	31	22.6	11.3
Average	67.7	45.5	28	12.1
Cow No. 4.—July 16	90	90	69	57
" 17	85	57	50	24
Average	88.5	73.5	59.5	40.5
Mixed Milk.—July 16	73	70	43	27
" 17	67	43	30	14
Average	70	56.5	36.5	15.5

The results from this work on cream raising by dilution, show (1) that with rich milk and with that from a new milch cow, the cream rose as completely when the new milk was quickly cooled to 70° F. without the addition of water as it did when diluted with an equal quantity of water.

(2) The rising of the cream was more complete in a given time, and was hastened by diluting the milk from cows that were not fresh or that gave a considerable quantity of average milk.

CAMPHOR: METHODS OF GROWTH AND MANUFACTURE IN FORMOSA.*

By Edward Bedloe.

The most interesting portion of my district of "Amoy and its dependencies," to use the diplomatic phrase, is the great island of Formosa. The name (the Portuguese adjective for beautiful) is extremely appropriate, for I question if any handsomer or more picturesque scenery can be found upon the globe. The territory is over 200 miles long and 60 wide, and is about as large as England, Scotland and Wales combined. Along its major axis runs a double range of magnificent mountains, several of whose summits are constantly covered with snow. The fertility of the soil is proverbial in the East. At some points the land produces from three to five harvests a year. Besides the best tea in the market, it produces unlimited quantities of camphor, sugar, rice, hemp, oil, oil cake, castor oil, turmeric and valuable woods. It ought to have an immense commerce with every part of the world, but it has not, which is due to the time-beaten prejudice of its governing classes against foreigners and everything foreign.

Nowhere does the force of this blind prejudice show itself in so large and ruinous an extent as with the trade in camphor and camphor wood. From the earliest times camphor has been a practical necessity to man. Its pleasant perfume, its destructiveness to insect life and its many remarkable therapeutic virtues have more than earned its great popularity.

In the past twenty years its importance has been multiplied many times by the discovery of celluloid, zylonite and smokeless powders, in all of which it is an essential ingredient. While the camphor tree grows in numberless places, it finds its best development in Japan, and, above all, in Formosa. In the last-named place it is the predominant forest growth. The trees upon the island are to be numbered, not by hundreds of thousands, but by millions. At the present time there is enough camphor in Formosa to supply all Christendom for a century. Yet notwithstanding these facts, the output of the entire island in 1890 was only about 60 tons!

The camphor expert selects a tree, and scrapes into the trunk in different places, using an instrument resembling somewhat in appearance a rake, with teeth of curved, gouge-shaped edges that

*From the Am. J. Pharm., Jan., 1892.

cut pulling. This scoops out the wood in little crescent-shaped chips. A tree is not considered to be worth anything for camphor purposes until it is 50 years old. The yield of a tree is unequal, being greater in and about the roots than higher up on the trunk.

The scrapings or chips are pounded in a stone or iron mortar and boiled in a large iron caldron, over which is placed, with the concave side covering the mouth of the caldron, an earthenware bowl-shaped vessel. In the boiling the camphor sublimes and condenses on the inside of the big bowl, which is removed from time to time, the camphor scraped off and replaced.

The root and trunk are scraped while the yield lasts, and the chipping is continued till finally the tree falls. No attempt is made to extract the camphor from the trunk or branches of the fallen tree. In some cases the trunk is sawed up into planks, but this depends upon the locality. In many districts, owing to absence of roads, timber would not pay for its transport. It is impossible to imagine a more wasteful method, and it is fortunate that the camphor forests of Formosa are practically inexhaustible. The quantity of camphor produced depends upon the amount of labor employed in the business. Ten iron pots and accompanying bowls make up what is called a "set," and are worked by four men. One set will produce about six pounds a day ; a fair average is 150 pounds a month.

At one time the camphor trade was monopolized by the Governor of Formosa and his official staff. The annual output ran as high as 250 and 300 tons and netted the distinguished syndicate over $100,000 a year. The profit can be easily appreciated when it is known that the poor peasant was paid four cents per pound for the camphor which was sold a week afterwards in Hong Kong for anywhere from 24 to 35 cents. The monopoly was abolished in 1870 at the intervention of the ministers of all the great powers at Peking. Foreign merchants, especially British and American, prepared to enter the trade on a large scale. The authorities, with characteristic shrewdness, enacted forthwith a likin or internal revenue system which completely frustrated all attempts to do business successfully.

(1) A tax was imposed upon every pot or boiler, no matter whether used full time, half time, or no time at all. As non-pay-

ment of a tax in China is a crime punishable by fine and imprisonment, this measure caused the camphor makers to break and destroy one-half of their plant rather than run the risk of going to jail.

(2) A heavy "battery tax" (or an assessment for the building and maintaining of forts in the district) was imposed upon the finished product. This was nominally about three cents per pound, but as levied came to twice that figure.

(3) The barrier imposts (or likin proper) were assessed at from one to two cents a pound upon the article. In instances a donkey load of camphor would be obliged to pass six to a dozen barriers between the point of production and the market place.

(4) An export duty was laid upon the camphor.

(5) A system of terrorization was set on foot by the subordinate officials, which frightened nearly all the camphor growers from selling to the foreign hongs. Under these circumstances the trade languished, and the supply demanded by Europe and America was drawn from Japan and other countries.

In 1885–86 there was a change in the administration of Formosa and a more liberal and progressive set of men came into office. They began their régime with promise of reform, of new laws for the extension and benefit of trade, and of a more generous and equitable treatment of the foreign hongs. The latter were delighted and made contracts with the native merchants and farmers for large quantities, to be delivered at the place of production and to be brought down to the port under the protection of official permits.

The first consignment arrived promptly and cleared a very handsome profit. The merchants were delighted, but their pleasure was short-lived, inasmuch as the new Governor, without a word of warning, re-established the old monopoly. Notwithstanding the contracts then pending between the foreign merchants and the native dealers, contracts upon which large sums had been advanced, the internal revenue and custom house officers seized all the camphor in the market or in transit, permits or no permits. The merchants were thunderstruck and appealed in a body to the British and United States Consular represenative at Talwanfoo, Hon. Pelham L. Warren, a brave and brainy gentleman. He made a strong fight against the outrage, put in claims for heavy

damages, carried the case to Peking, where he was sustained by the united foreign legations, and afterwards by the highest authority in China, the Jsung-li-Yamen or Imperial Cabinet. The monopoly was expressly abolished, and the claims after tedious delay and litigation, allowed and paid in full to the sufferers.

Before the opportunity thus created could be taken advantage of, the local administration levied a special tax on camphor of one cent per pound, exclusive of the internal revenue and export duty. It was done under the pretext of a "garrison tax," the Government claiming there was danger of an uprising of the savages in the interior of Formosa, and that new regiments had to be raised, equipped and supported. There never was any uprising, there were no troops recruited, but the tax ran gayly along all the same, and the proceeds went into the pockets of those in power. The tax was then raised to two cents per pound as the price of camphor rose in the Hong Kong market, and as this did not change the state of affairs it was again raised, this time to 13 cents per pound. At the same time the camphor growers were warned by threatening proclamations that they were required to pay this tax in advance upon all camphor produced; that any delinquency or mistake would meet with the severest punishment, but that the "camphor farm" (a new form of the old Goverment monopoly) would pay eight cents a pound to any and all growers for their crop. Up to the time of these last enactments the price of camphor had fluctuated in the country where it is grown from four to eight cents a pound. It now rose with a jump to 21 cents. The net return to the buyer was about five cents on an average; the difference went to the "camphor farm," that is to say, about one-tenth thereof to the members of the official clique and nine-tenths to the superior officials of Formosa.

The monstrous condition of affairs has remained unchanged up to date. The producers are afraid to deal with the foreign merchants lest they be fined and imprisoned for some technical violation of the law. The merchants are fearful of making contracts which will cause litigation and loss at the hands of the internal revenue and the customs. The trade has, therefore, been steadily falling off, and as the smokeless powders of Europe, made from camphor, have proved to be failures, and are being replaced by explosives in which that substance is not employed, the demand is

diminishing from abroad, so that there is every prospect of an utter collapse of the camphor trade and the camphor monopoly in Formosa.

The monopoly is singularly devoid of intelligence. The Chinese never dare to go into the interior, where the savages live, and where the finest camphor can be had at almost no expense.

The savages, strange to say, have a wild love for Europeans or white people, probably because of their hatred for their Chinese enemies, and are willing to supply any amount of camphor on demand. The monopoly, to prevent this source of competition, have had a law passed prohibiting all intercourse or commerce with the aborigines, and even forbidding the tourist to enter the latter's territory. There is at present some prospect of a speedy change. The old Governor has just been removed, and a new one is to be appointed. In view of the serious troubles in China, which are forcing the Central Government into more intimate and more amicable relations with the foreign powers, it is more than probable that the coming appointee will inaugurate a wiser and better policy than that which has prevailed in Formosa during the past five years. If such an event occurs, there will be a wonderful development in the commerce of that wonderful island. For it will sink deeper in the ocean of bankruptcy and poverty.

NEW BOOKS

Trimble's The Tannins. [illegible]

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ON THE MANUFACTURE OF THE CINCHONA ALKALOIDS.

BY WALTER D. FIELD.

PART I.

The manufacture of quinine, quinidine, cinchonine, and cinchonidine has been one of great progress.

Manufacturers have jealously guarded their secrets in their endeavors to cheapen the production. With the drop in prices from about $3.25 an ounce in 1880 to about 26 cents an ounce in 1892, the questions naturally arise: Are the manufacturers losing money? Was there a cause other than competition that brought about the fall in prices?

Undoubtedly competition caused the manufacturer to bestir himself to find cheaper and better methods for extracting the alkaloids. With what success no better testimony is needed than the present selling price of the alkaloids.

In this paper, the writer will endeavor to show how to extract the cinchona alkaloids from the bark and how to separate them from each other in an economical manner.

THE SEVERAL METHODS OF EXTRACTION.

The use of alcohol was too expensive. Besides, the alcohol extracted a large amount of coloring matter and rendered the separation of the alkaloids from each other difficult. Large quantities of bone black were necessary to decolorize the solution of the alkaloids, and the loss was heavy on account of the amount of alkaloids which the bone black absorbs and which is difficult to

reclaim. More will be said upon this subject when the separation of the alkaloids is taken up.

The extraction of the bark with dilute hydrochloric or sulphuric acids is open to the same objection as the alcohol process and further, because they *will not* completely exhaust the bark. Dr. Vrij[illegible] says that dilute sulphuric acid will not extract the bark. It is also true that dilute hydrochloric acid will not extract the alkaloids completely on a commercial scale. Extraction by means of dilute acid was nevertheless the method in use for a long period of time.

Turpentine has been tried without success; fusel oil and benzine with some success. Turpentine will not exhaust the bark; fusel oil, when used alone, is apt to leave an odor in the finished product.

Tribouillerie first used petroleum oil, but no one seems to have thought of utilizing it in the practical manufacture of the cinchona alkaloids. It remained unused until later times, when it was used in combination with fusel oil to extract the alkaloids. Far better results can be obtained with a combination of fusel oil and petroleum oil than with either alone. This fact is not unusual; combinations of liquids having been known to be better solvents than either of the combined liquids used alone. For example, it is well known that though neither ethyl alcohol nor ether (ethyl ether) will dissolve pyroxyline, yet when combined in equal volumes they become a powerful solvent of that substance.

ANALYSIS

The manufacturer will always find himself safe in getting a correct estimate of the value of his bark by using in miniature the method followed by him in commercial extraction.

The methods [illegible] and petroleum oil are used as follows:

Take [illegible] grams of bark [illegible] grams slaked lime, mix [illegible] and moisten [illegible] with water to a stiff paste and [illegible] the liquors [illegible] longer [illegible] get [illegible]

ting *hot* slacked lime. When the lime and bark are mixed, add three-quarters of a pint of a mixture of 25 per cent. fusel oil and 75 per cent. coal oil, or petroleum oil, 150° test. This mixture must have time to settle, as water is precipitated from the fusel oil on adding the hydrocarbon oil. Domestic fusel oil contains about 7 per cent. water in solution. This is not entirely precipitated by the dilution with a hydrocarbon oil.

After adding the three-fourths of a pint of mixed oil, boil on a water-bath, in any suitable vessel, for three-quarters of an hour, then transfer the bark and oil to a percolator, let the oil run into a bottle, with a ground glass cock in the bottom. Then wash bark in percolator with three-fourths of a pint of hot mixed oil, allowing to run off slowly. Return bark to digester and boil one-quarter of an hour with three-fourths of a pint of mixed oil. Again transfer to percolator, allow to run off rapidly, and wash with three-fourths of a pint of hot mixed oil.

Now add six ounces dilute sulphuric acid (1 in 20) to the mixed oil extract, and then shake well. Allow the liquid to settle one-half hour to insure complete separation, then remove the acid solution by drawing off through the glass cock in the bottom of the bottle.

Shake the oil a second time with an ounce of sulphuric acid (1 in 20); this removes the last traces of alkaloids. Mix this with the first six ounces used, in an evaporating dish, heat to 95° C., then neutralize with decinormal soda solution, and allow to cool. Filter the crystals which separate, and wash with a small amount of cold water, then dry at a temperature not exceeding 90° C. Test the dried crystals for ether-soluble alkaloid with Liebig's ether test.

The amount of soluble alkaloid obtained thus should be taken as a basis for calculation by the manufacturer using the process of manufacture given in this paper.

If a more complete analysis is desired, proceed thus: After neutralizing the acid extract of the mixed oil, add one ounce of a saturated solution of rochelle salts, allow to cool; the quinine and chinchonidine crystallize out as tartrates; filter, wash, dry, weigh, taking same precautions as before noted in these operations. Take 0.65 gms of the mixed tartrates and dissolve in 30 cc. 95 per

cent. ethyl alcohol. Add just sufficient (about 5 drops) sulphuric acid (1–5) to decompose the tartrates, then proceed with De Vry's iodo-sulphate chinoiden test.

E. Landrin[4] gives a similar method: 300 gms. of the bark are powdered and passed through a No. 40 sieve, then mixed thoroughly with 1 liter of milk of soda lime containing 75 gms. of quicklime and 75 gms. solution of sodium hydrate at 4° B. To this mixture thinned with a little water two liters of petroleum spirits are added, heated to 100° C. for twenty minutes, with constant agitation; the oil is then decanted and the extraction repeated with a second two liters. The four liters of extract are washed twice with 75 cc. of 10 per cent. sulphuric acid added to 150 cc. water, and a third time with one-third this quantity. On cooling, about nine-tenths of the alkaloidal sulphates crystallize out, are filtered off, and the mother liquid precipitated by sodium hydrate, the alkaloids washed, dried, pressed, and transformed into sulphates by cautious addition of sulphuric acid, then added to the rest and weighed."

The author says he has followed this process for some years with good results, and I am inclined to think as he does.

The first method which I have given extracts but little of the coloring matter, not enough to interfere with the method. The alkaloids crystallize pure white from the neutralized extract of the oil.

In general, the manufacturer who wants to know how much sulphate of quinine a bark will yield him will follow in miniature the process used by him on the large scale.

[illegible]

The bark must [illegible] enough to pass through a No. [illegible] [illegible] the case of the extract [illegible] taken to prevent the bark [illegible] the mass in which the [illegible]

[illegible] M. [illegible] at w[illegible] [illegible] in the [illegible]

Therefore mills with contact plates are not desirable, as they cannot be used for every bark. Unless the mills are enclosed, they should be made to discharge into a closed bin, still, as a second precaution against dust, the grinding room should be exhausted by means of a fan or blower, in the manner of a planing mill, into a closed chamber in which a spray of water is being injected to collect the dust. The bark before being put into the mill must be broken up in a cage mill.

The Bogardus mill is a good one for grinding all kinds of barks; its action is rather one of cutting than crushing. The knives do not come in contact with one another, and hence do not heat the bark to any great degree.

Alsing's cylinder has many advantages. It will powder the bark as fine as necessary, without the dust flying into the room; it can be run in water and thus kept cool if it should become heated. The milk of lime can be added directly to the powdered bark while in the cylinder, and thoroughly incorporated with the bark. As "tumbling" is the best method for thorough mixing, the Alsing cylinder combines many good points in its mode of operation. Figure I gives a view of the cylinder and shows the manner of operating. It is driven by means of a belt and gear, thus insuring steady revolutions. The bark is introduced through the manholes *a* and *b* together with the iron or porcelain balls to be used in grinding. When the charge is ready to be discharged, the manholes *a* and *b* are replaced by gratings fine enough to retain the balls. By revolving the cylinder, the charge can be emptied into a car beneath.

"The Abbe Mill" has been used with success in sugar grinding, and from its construction, I should think it would prove a successful mill for grinding cinchona bark.

EXTRACTION OF THE BARK.

The bark having been ground, is thoroughly incorporated with 20 per cent. by weight of slacked lime. This is an important step in the process, and must be done in a thorough manner. "Tumbling" will do this better than any other way, and thus insure a perfect extraction. The workman in charge of the mixing cylinder should not be allowed to decide when the charge

is done, but should always submit samples to the superintendent for his decision.

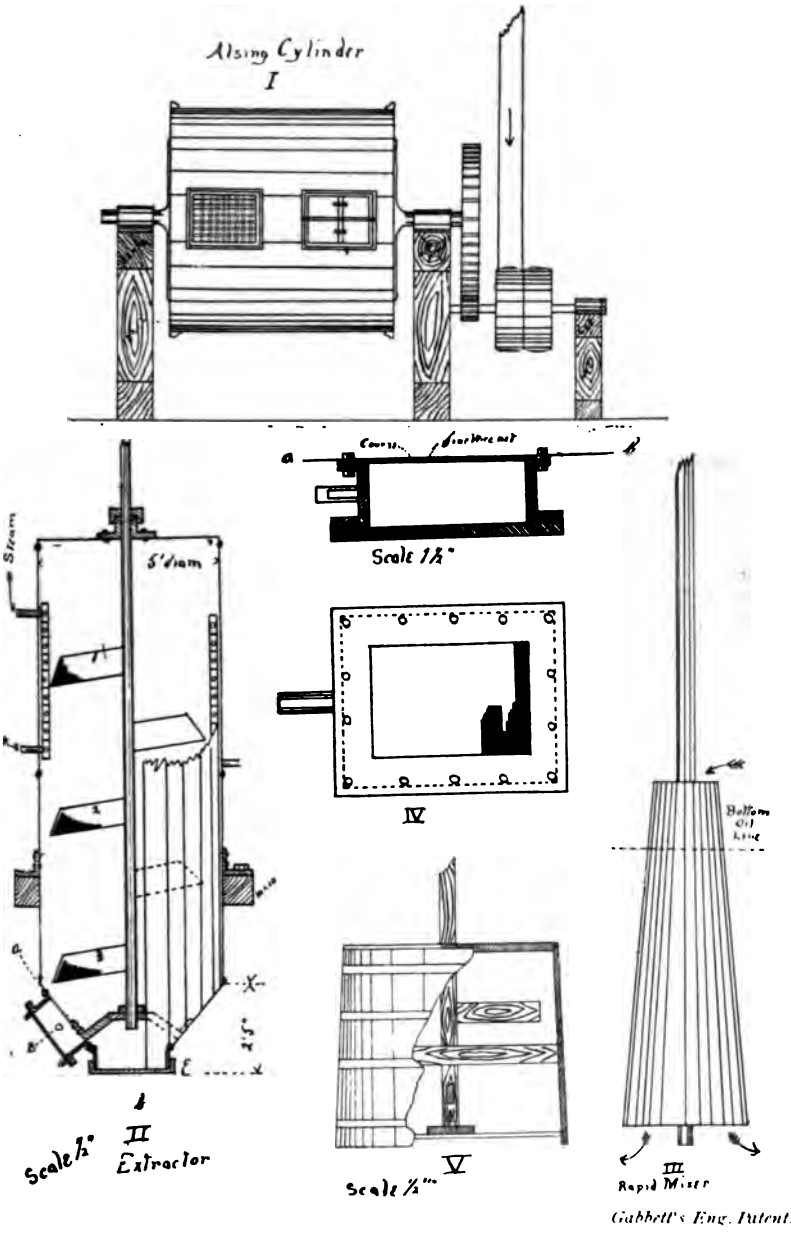
The lime is in the form of stiff paste, and should be slacked some time previous, so as to allow of its getting perfectly cold.

After mixing with lime, the bark is transferred to the extraction apparatus, represented in section by Fig. II. This apparatus is able to extract nearly a ton of bark per day of twelve hours, and requires for this purpose about 3500 gallons of oil, consisting of kerosene oil, 75 per cent; fusel oil, 25 per cent., (the kerosene and fusel must be mixed before use, and the separated water allowed to settle), divided into four charges of about 900 gallons each. In the upper half of the extractor is placed the steam coil. This arrangement brings the line of the bark after settling below the steam coil, and prevents the lime from burning on the coil.

The mixing of the bark and oil is another important step, in fact, is the important point in the manufacture of the cinchona alkaloids. It must be done perfectly, or else the yield of alkaloids will fall below the estimated amount. To do this requires an agitator that will bring the oil and bark in contact and keep them moving together while heating. An agitator consisting of a shaft on which broad iron arms are bolted, twisted sufficiently to give the bark an upward motion into the oil, is represented in Fig. II. A mixer patented in England, and now being made and sold there, is an excellent one for this purpose. It is shown in Fig. III. The cone can be used the opposite way from that shown in the drawing, in which case the direction of circulation of the liquid is reversed.

Another simple but effective way is to use the method of mixing as given in Fig. V, in which the arms extend clear across the extractor at right angles to each other, and between them is placed a flat piece of iron bolted to the sides of the extractor. This will be found a general way of doing all the mixing required during the extraction and separation of the alkaloids.

To remove the oil from the bark after the agitation is complete, an exhaust pump is used. Fig. IV shows in detail the section *a*, *b* in Fig. II. It consists essentially of two iron nettings bolted tight against the side of the extractor by means of an iron framework. One of these nettings is very coarse and heavy, and is put



Gabbett's Eng. Patent.

on the outside of the fine netting, thus keeping the weight of the bark from tearing the fine netting and the exhaust pump from bulging it. Another similar attachment can be put on the opposite side of the extractor if desired.

The first two extractions of the charge are run into the washing tank, the last one or two, as the tests have found to require, are run into another tank and used for the first extraction of a new charge. A charge of bark should never be removed from the extractor until the superintendent has tested it by extraction of a sample in the laboratory, or washing with dilute sulphuric acid a sample of the last charge of oil, and precipitating the alkaloids with caustic soda solution.

The test having proven the bark completely exhausted, the exhaust pumps are run until all the oil is run off and the residuum is discharged from the extractor through the manhole *l* into a car or pit. It is evident that the oil cannot be entirely exhausted from the bark, but the loss is slight and could not profitably be recovered.

The first two portions of oil used for the extraction are run into a tank, such as given in Fig. V, where it is treated with the dilute sulphuric acid [illegible]. Six to eight ounces of dilute acid are required to about one and three fourths gallons oil. Five gallons of dilute acid to every hundred of oil are good proportions.

The washing tank is lined with [illegible] lead and provided with a lead cock burnt into the lining as near the bottom on the side as possible. The lead cock had better have a ground porcelain plug, [illegible] than any other form that can be used in this place.

The [illegible] neutralization and the first crystallization. It [illegible] before this step to allow the [illegible] standing one or more days in a settling tank [illegible] to separate out.

The [illegible] analyzed for [illegible] the bark and also the finished product [illegible] should be [illegible] estimates [illegible] the alkaloids can be kept [illegible].

[COMMUNICATIONS FROM THE CHEMICAL LABORATORY OF RUTGERS COLLEGE.]

THE UTILIZATION OF THE ELECTRIC LIGHT CURRENT FOR QUANTITATIVE CHEMICAL ELECTROLYSIS.

BY JOSEPH S. STILLWELL AND PETER T. AUSTEN.

To apply the electric light current to electro-plating and chemical determinations, and to do this by the simplest means and in a manner adapted for use in chemical laboratories, was a problem, the solution of which would afford so great a convenience in the practice of analytical chemistry, that we deemed it well worth study and investigation.

The use of electricity for the purpose of quantitative analysis is of recent date. Its advantages as summed up by Dr. Alexander Classen in the preface to the second German edition of his work on this subject, entitled "Quantitative Chemical Analysis by Electrolysis," are as follows: "This new method of analysis may now be considered as established in its essential points. The great advantage of quantitative electrolysis, apart from its greater simplicity, lies unquestionably in the fact that the electric current does the work of the analyst, setting him free to carry on other work. Experience has shown that if the methods are correctly followed out, even unskilled analysts obtain results that experienced chemists can with difficulty reach with the ordinary methods of gravimetric analysis."

The first essential for electrolytic work is a current generator, and the practical value of electrolytic methods in general laboratories depends much upon the ease and cheapness with which the current is produced. There are three classes of generators in use, the thermopiles, galvanic batteries, and magneto-electric machines, or dynamos. The first class, the thermo-electric piles of Clamond and of Noe, are not in general use, and Classen's experience with them does not favor their application to analytical work. He says: "They do not give a current strong enough for most determinations and separations, and are liable to fail after continued use, and then can be repaired only with difficulty, often not at all."

Galvanic batteries are in common use, and have the advantage of low first cost, of being easily portable, and when a number are to be had, of furnishing currents sufficiently strong for all purposes

of analysis; but they have also the accompanying disadvantages of inconstant current, of requiring refilling, and, with zinc cells, of amalgamation, of giving off offensive fumes, and when the electrolytic work of a laboratory is not of sufficient magnitude to warrant constant care of the cells, the labor and inconvenience of setting up the battery will generally offset any advantages that this method possesses.

Dynamic currents, or currents from magneto-electric machines, constitute the third class. Their use implies either the possession of a dynamo and power to run it, or else the use of wires from one located elsewhere. When power is at hand, it may be convenient to use a small dynamo, but even this demands care and adjustment. It cannot be left to run over night, and the first cost is an important factor.

The electric light system has now been fully established as one of the institutions of our civilization; and there is hardly a city of any size in the country where the central station and its radiating system of wires may not be found. It can consequently be easily introduced into nearly all of the prominent laboratories, where its use is by no means confined to simple illumination, but may also be applied to replace the calcium light, to run small motors, and to furnish electric currents of convenient strength for electrolysis or other purposes. Any system of electric lighting, even arc light systems, can put in two wires conveniently located, between the terminals of which there will be a difference of potential, which, although comparatively high (in our country in nearly all systems about 110 volts), will not be at all dangerous to handle; a safety plug with a lead large enough to convey power to run only nine sixteen candle power lamps will guard against accidents.

The difference of potential between the wire terminals will be high, that is, high compared to the potential of batteries or small dynamos, and to reduce the large current, which, according to Ohm's formula—

$$C = \text{Current} = \frac{\text{Potential} = E}{\text{Resistance} = R}$$

is consequent upon this high potential, was the object to be attained.

The particular system of electric lighting used in New Bruns-

wick, and furnished to the College Laboratory, is the "Edison three-wire," or "neutral wire" system.

In this there are three main wires, and consequently three branches are led into the building. These terminate over the laboratory desk, after being conducted through several sockets, either for the introduction of lamps or plugs, and by means of binding screws at the terminals, the wires may be connected and the current "put on." The connection should not be made, however, unless some resistance greater than that of the armature of the generating dynamo is in the circuit; otherwise, what is called "short circuiting" occurs, and something must give way, either the plugs are "burned out," or if the voltameter happens to be in circuit, the small platinum wires of that instrument are melted. Either occurrence involves trouble and delay. The current also should not exceed the capacity of the leads in the plugs, which for nine sixteen-candle power lamps is 4.68 amperes. The resistance of the armatures used in very high potential systems (arc light) may run as high as 20 ohms; of low potential (110 volts) systems, four or five ohms may be considered the maximum. Suitable safety plugs should, of course, be provided, but for electrolytic work, however, no higher than a No. 6 plug is demanded. The high potential of the town current necessitates the use of resistances; coils of German silver, or other high resistance wire, are the usual means employed for reducing current, but they are subject to the attacks of the laboratory fumes, and thus become coated and unfit for use. The use of solutions of zinc sulphate and other salts as resistances is subject to the same disadvantages which attend the use of batteries as generators. Counter electro-motive force was tried, and a series of cells consisting of test tubes furnished with lead strips and filled with dilute sulphuric acid, was put in circuit. Each cell then gave a little over two (2) volts potential, and thus the potential of the town current could be opposed and changed at will, but the spray from the tubes attacked the connections and rendered the current inconstant.

Simplicity, high resistance, durability under the injurious influences of a laboratory atmosphere, were the requisites demanded in the means used to reduce the current; all these advantages were found in the incandescent lamp, to which may also be added the advantage of cheapness, for "blackened lamps" (the blacken-

ing caused by carbon from the filament settling on the glass [illegible] as yet among the waste products of the electric light system and can be obtained for little or nothing at any incandescent station.

The "life" of a sixteen candle power lamp was formerly estimated at [illegible] ohms, after that the blackening of the glass or the breaking of the filament rendered it unfit for use. Lamps have of late been much improved in this respect. The resistance of these lamps is very high, varying, however, with the candle power and the time they have been subject to a current strong enough to make them glow, this latter a small change. They also vary in their resistance according to the period of their manufacture, lamps of an older pattern having a much lower resistance than those of later "make." The resistance also changes with the temperature of the carbon filament; thus a lamp of [illegible] ohms resistance when cold had a resistance of [illegible] ohms when at a white heat, the resistances varying with the temperature between these two extremes.

Following we give the resistance of a number of lamps.

[illegible]

No.	[illegible]	[illegible] ohms	[illegible]
[illegible]	[illegible]	[illegible]	[illegible] incandescent	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

The resistance when cold of numbers [illegible] and [illegible] is nearly the same [illegible] But when placed in [illegible] current of [illegible] volts No. [illegible] gave [illegible] amperes per [illegible] ohms and No. [illegible] gave only [illegible] amperes [illegible]

[illegible]

[illegible] lamps were [illegible] incandescent. A [illegible] R [illegible] ohms R [illegible] at a white heat [illegible] lamps was as [illegible]

[illegible]

No. [illegible] sixteen [illegible] lamps [illegible] resistance

are for blackened lamps. The resistances of new night lamps were found to vary from 750 to 800 ohms when cold. The above resistances when cold were measured with a galvanometer by the Wheatstone bridge method, when hot, with the voltameter, calculating from the current indicated. The voltameter will give results accurate enough for electrolytic work, for Classen says: "A current of a certain *exact* strength is not required for a quantitative determination, or separation;" in fact, it is only for this reason that it is possible to conduct analyses by electrolysis without great difficulty.

The resistance of two lamps, of equal resistance when hot, when arranged in series and exposed to a current of 110 volts, is greater than twice the resistance of one, as, when one is singly exposed to the current, it is at a higher temperature, and hence has less resistance than when it has a companion to share the force of the current. Thus, two 50 c. p. lamps, when placed in circuit alone, each gave about 3.1 amperes, the carbons being at a white heat, but when placed in series, the carbons were only a bright red and the current was 1.13 amperes, a little over a third instead of half the current let through one lamp. The measure of current as read directly from the voltameter is the cubic centimeter (cc.), it is equal to .0958 ampere. It should be remembered in calculating that the current in cubic centimeters must first be reduced to amperes before it can be substituted in Ohm's formula. Roughly approximating, 10 cc. equal one ampere.

The currents required for quantitative chemical analysis vary with the metals to be separated or determined. According to Classen, a solution of iron oxalate requires a maximum current of 20 cc. per minute, while bismuth is thrown down from a like solution by a current of only 0.1 cc. The currents required vary also with the solution used; thus, copper in nitric acid solution requires 4 to 5 cc per minute; in the oxalate solution, 0.1 to 0.2 cc. only. Ammonium oxalate solutions of iron require 15 to 20 cc.; of cobalt and zinc, 8 to 10 cc.; of tin, 10 cc.; of manganese, 9 to 10 cc.; copper and cadmium, 0.2 cc.; silver in potassium cyanide solution requires 1.5 to 2 cc. The above examples are specimens of the strengths of currents demanded, and are applicable to the size of electrodes commonly used in quantitative electrolysis, *i. e.*, platinum dishes, cones, and cylinders.

All of the above mentioned currents have been obtained by the use of incandescent lamps as resistances in the current of the electric light system. Moreover, the currents thus obtained are constant, they are always at hand, and can be turned on by the movement of a switch; they can with safety be left to operate during the analyst's absence, or over night, something which can rarely be done with batteries or dynamos. The lamps used in the experiments for the reduction of the electric light current were 50, 32, 24 and 16 candle power, all blackened; also some new night lamps, which, however, can very rarely, if ever, be obtained in a blackened condition. The same remark applies, in a lesser degree, to 100 c. p. lamps. These, therefore, if desired, must be purchased, but the others will answer all purposes. Their resistances and the causes of their variation have already been given.

The following currents have been obtained by the use of lamps in series (in some cases a single lamp); the 110-volt current was the one used; if, however, it be necessary, the 220-volt current can be put on and the currents given below somewhat more than doubled, according as the larger current heats up the filament, and thus lessens the resistance. Unless otherwise mentioned, the lamps used were all blackened.

33 cc. were obtained by introducing into the circuit a new 100 c. p. lamp of new pattern.

31	cc. by	a	50 c. p. lamp,	old pattern.	
25.5	"	"	50 " "	new	"
24	"	"	50 " "	old	"
18	" (by means of side currents)				
16	" by	a	32 c. p. lamp,	new	"
13	"	"	24 " "	old	"
11.4	" by	(2)	50 " lamps,	"	"
10	"	"	50 " "	new	"
8.4	" by	a	50 and a 32 c. p. lamp.		
7.2	"	" (2)	32 c. p. lamps,	new	"
6.2	"	" a	32 and an old pattern 24 c. p. lamp.		
5.6	"	" (2)	50's and a 32 c. p. lamp.		
4.4	"	" (4)	50 c. p. lamps.		
4.2	"	" (3)	32 " "		
3.7	"	" (2)	32's and an old power 24 c. p. lamp.		
2.8	"	" a	24 c. p. and (2) 32 c. p. lamps.		
1.05	"	" (6)	25 c. p. lamps.		
0.64	"	" (5)	16 c. p. lamps.		

For currents much below one cc. per minute, the resistance required is very high, and hence demands a number of lamps of high resistance. Thus, taking 1 ampere equal to 10 cc. to obtain a current of 0.1 cc., or 0.01 ampere, a resistance of 11,000 ohms must be put in the 110-volt circuit, as will be seen by the formula

$$C = \frac{E}{R}$$

or substituting $0.01 = \frac{110}{R}$ $\qquad R = 11{,}000$ ohms,

to obtain a current of 0.2 cc. would require 5500 ohms; of 0.3 cc., 3660 ohms; of 0.4 cc., 2750 ohms.

Now as the resistance (cold) of night lamps is about 750 ohms, and of blackened 16 c. p. lamps about 400 ohms, it will be seen that whichever is used, a large number (of night lamps 16, of 16 c. p.'s, 30) will be required for a current of 0.1 cc. This would be troublesome, hence, an expedient was resorted to which not only enabled us to obtain very small currents with but few lamps, but also to obtain several currents varying widely in strength (from 20 to 0.1 cc.) at the same time. The above-mentioned limits can be increased, if necessary, but they are the extremes demanded for electrolysis with the usual apparatus.

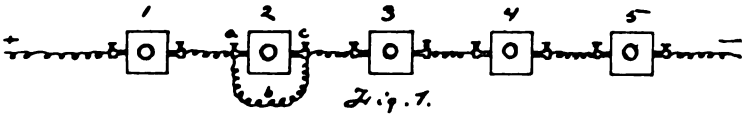


Fig. 1.

This expedient and the principle upon which it depends may be explained by the aid of the accompanying figure (Fig. 1). Let "1, 2, 3, 4, 5" represent a series of lamp-sockets on the circuit + —; suppose each socket to be furnished with binding screws, so that a side current as *a*, *b*, *c*, around socket 2, can be taken around it. Suppose, also, that five lamps of equal resistance be screwed in the sockets, and the 110-volt current be passed through the circuit. Then the potential of the side current *a*, *b*, *c* will be a fraction of the potential of the main current + — whose enumerator

is one and denominator the number of lamps the lamps being [illegible] equal resistance. In this case we have five lamps in circuit hence the potential in the side current over one lamp is one fifth [illegible] volts, or 22 volts. Now this side current can be dealt with as an independent current, and as the potential or numerator in the equation

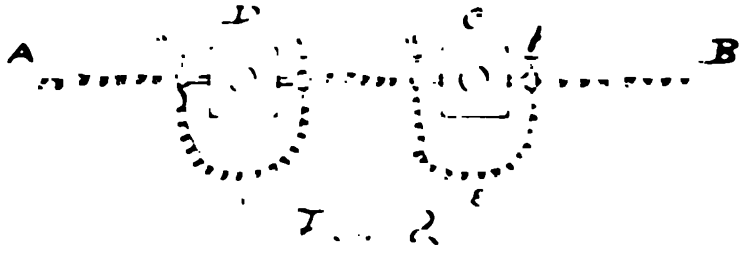
$$C = \frac{E}{R}$$

becomes for this current 22 volts, as against 110 volts in the main circuit this current can be reduced with one fifth the resistance required to produce the same effect in the main circuit. Hence only three eight lamps or six sixteen candle power lamps are required to reduce this side current to [illegible] per [illegible]

$$C = \frac{22}{R} \qquad R = \frac{22}{C} \text{ ohms}$$

R [illegible] three eight lamps [illegible] 22 ohms

In the above example the resistance of the lamps is taken as equal but if the lamps are placed in series the resistance of the first lamp [illegible] current [illegible] Here [illegible]



ohm lamp *C* will be one-fifth of 110 ohms, or 22 ohms; hence, this latter circuit will give the smaller current for equal resistances in the proportion of 1 to 4. It is easily seen that by increasing the number of lamps in the main circuit, several side-currents can be operated, or side-currents can be taken around lamps which are in other side-currents, and the potential carried to an infinitesimal if desired. By placing three 50-candle power lamps in the main circuit in series, and introducing in the side-current around one of them three (3) night lamps, and carrying a plain wire of no resistance around another, we obtained in the night lamp circuit a current of 0.22 cc., and in the plain wire circuit a current of 11.4 cc., or 51 times as large.

If very large currents are desired, say from 4 amperes up, 50-candle power lamps may be placed in parallel, each lamp will let through from two to three amperes, according to the pattern. Side-currents may be taken from these lamps, and resistances introduced as usual, thus allowing the simultaneous running of larger and smaller currents than can be obtained by the series arrangement.

With two currents of different strengths running at the same time, the increasing of the smaller, or side-current, was not found to diminish the larger, or main current. Thus, when the main current was 11.4 cc. per minute, the side-current was increased by the subtraction of resistances from 0.22 to 6 cc., without any sensible effect on the main current.

The following diagram and explanation will describe the arrangement of lamps and wires necessary to obtain current sufficient for quantitative electrolysis. The whole apparatus can be made from a few yards of insulated copper wire, some 16 wooden lamp sockets, and blackened lamps, say six 50-candle power, three 32-candle power, six 24-candle power, and six 16-candle power. Night lamps may also be added, but as they are rarely returned to the stations in a blackened condition, old ones cannot be obtained, and new ones must, of course, be paid for. The above outfit will, however, answer all purposes. Some binding screws, connections, and plugs will also be necessary in addition to those which are put in with the electric light wires.

The main wires +, +, — (Fig. 3), are furnished with sockets *A*, *B*, *C* for the introduction of safety plugs, which, for the small currents used in electrolytic work, need not exceed 6 lamp leads. The main wires terminate in binding screws, by which they are

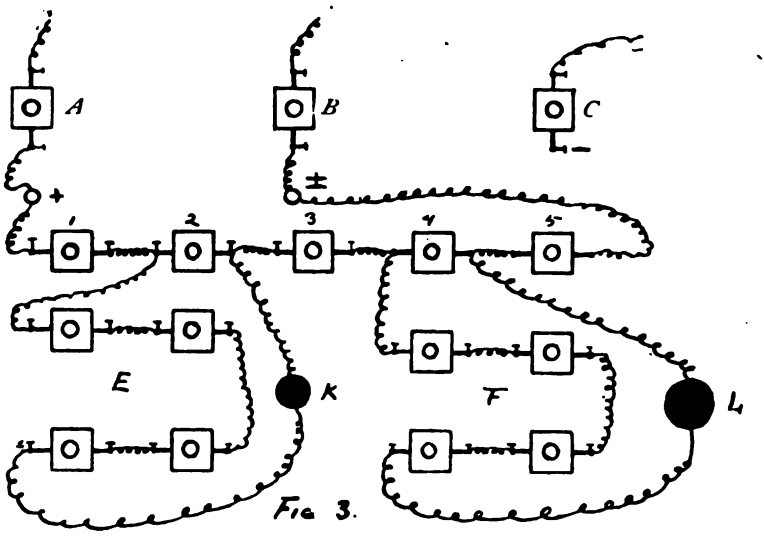


Fig. 3.

connected with the series of sockets 1, 2, 3, 4, 5. In these the lamps for reducing the main current are placed, and if only one determination or like determinations are required to be made, only this series will be necessary if ordinary currents are required. If, however, two or three different determinations, or some requiring very small currents are to be made, side-currents can be formed, as around sockets 2 and 4, and the current brought to the desired size by the introduction of resistances in the series of sockets *E* and *F*; *K* and *L*, will represent the proper position of the solutions to be electrolyzed by these side-currents.

By this arrangement three unlike determinations can be simultaneously made, one in the main circuit, and one in each of the side-series. It is not probable that a large number will be required to be made at any one time, but if such should be the case, other sets of sockets may be put up and potentials be taken over other lamps. The sockets may be placed on the wall above the desk, the wires leading down to the solutions to be electrolyzed.

This seems to be the most convenient arrangement, but others may be adopted, as best fitted to the place or operation, or as suited to the taste of the operator. The above arrangement can also be adapted to the parallel system by breaking the connection of the sockets used, with each other, and connecting each one separately with the binding posts of the main wires.

The current, as described above, comes from the Edison "three-wire" system. The wires of any other incandescent system may, of course, be used, and the plans given here will apply as well, save that the neutral wire is a feature of the Edison system. The lamps used in these experiments were all of the Edison pattern. The resistance of lamps of other makes will, of course, differ. However, it is an easy matter to determine the resistance of a lamp, and when once found, the lamp can be marked, and will remain a practical standard for some time. The lamps which we have used constantly in our experiments for some months have not sensibly changed their resistance. It should be remembered that there is a constant tendency to increase the resistance of incandescent lamps, and thus cheapen the cost of illumination. It is expected that the resistance may be doubled for the same candle-power lamp. For the taking off of side-currents, lamps of low resistance are needed in the main current, in order not to weaken it too much; hence, old patterns of 100 and 50-candle power lamps should be sought for this purpose, as they have lower resistance than newer patterns.

The cost of the electric current may be placed at about one cent per hour for a current of three-quarter ampere, or 7½ cc. As most determinations do not require a current much exceeding this, it cannot be called expensive, even setting aside its other advantages of convenience, etc. In view of the contemplated increase of resistance in the carbon filament, it may be expected that the cost of the current may be considerably lessened.

It was not our purpose to enter upon the investigation of quantitative electrolysis, as given by Classen himself. His name is sufficient to vouch for the excellence of his methods. We, however, have endeavored to furnish a means that would render the prosecution of these methods of analysis an easier task than when the chemist is dependent on batteries and other generators requiring care and expense, and we are convinced that the electric light current will answer this purpose.

A number of analyses were made, more for the purpose of acquiring a knowledge of manipulation, and the other practical details of analysis, than to attempt to demonstrate the utility of the electrolytic methods. The results were very satisfactory.

The advantages of obtaining a current from the electric light wire and of using lamps as resistances in quantitative electrolysis may be summed up as follows:

1. The current is convenient, requires no care to keep it in working order, and no labor to set it in operation.

2. Any current can be obtained by the use of lamps from [illegible] amperes down to a hundredth of a cubic centimeter and [illegible] still, if desired.

3. The cost of setting up and maintaining is small.

4. Incandescent lamps furnish an easy and reliable means of controlling the current, and they are not subject to the changes resulting from fumes, heat, and spraying, which injure rheostats and other metal appliances.

5. The current is steady and when once arranged can be left with the assurance that no weakening or stoppage will take place; hence, analyses can be run during the night, and the analyst can return in the morning sure that the current has accomplished the end designed.

A PROCESS FOR THE REMOVAL OF THE LINT FROM COTTON SEED

[illegible]

The [illegible] cotton [illegible] seed which [illegible] United States [illegible] adhered to the seed.

[illegible] extraction of the [illegible] States the great [illegible] [illegible] pressed.

[illegible] American seed much

"meat" is lost by becoming entangled in the hulls and failing to separate; on this account the oil-yield is lower by several gallons per ton than that from the naked seed, and the yield of "cake" is less as it contains no hulls. The American seed will not stand storage nor shipment well (especially export), as moisture absorbed by the fibrous envelope will enable fermentation to set in.

The process for the treatment of American seed is briefly as follows: They are (1) run through "linters," which remove as much as possible the cotton which has been left on the seed by the gin; (2) decorticated by a machine which cuts the seed-coat, whereupon the "meat" and the "hulls" fall apart; (3) separated by passing through an inclined revolving screen having meshes which allow the "meat" to fall through, while the "hulls" are retained and roll out at the lower end; or by means of an air blast; (4) the "meat" is heated and pressed. The hulls are burned, and the ash, rich in potash, has a market value.

All mechanical methods which have been devised to strip the seed of its fiber have proved unsuccessful, either from imperfect performance or lack of speed.

The chemical process described below was devised some time since (U. S. Pat. 344,951) by the author and N. W. Perry, E. M. It has never been tried commercially, but its success is perfect on a small scale.

The seed after linting are subjected to the action of N_2O_3 and SO_2, either in the above order or mixed together; enough air attending them to "regenerate" the NO. This is probably best accomplished by having the seed descend a chute slowly through which a current of N_2O_3 is ascending, and then into a chute where SO_2 and air are ascending; or they may descend through a chute having an ascending current of N_2O_3, SO_2, and air. After a few seconds' exposure to these gases under proper conditions, the fiber on the seed has changed very little in appearance, but its structure is so completely destroyed that the slightest friction causes it to fall into an impalpable powder. The seed are left perfectly smooth, showing no signs of corrosion. They have a slight acid reaction on the outside, but the acid is speedily removed by washing. The seed-coat is very hard, and is impervious to the gases. No trace of acid has ever been discovered in the interior. The seed germinate very quickly if planted. The acidity may also be removed

by blowing lime dust on the seed as soon as they come from the "cleaner" which removes the disintegrated fiber, or they may be carried by a conveyer through lime water and then through a dryer. The seed are now ready to be crushed and pressed or they may be shipped and stored as well as Egyptian or "sea island" seed.

The "cleaner" referred to above may be any good grain cleaner. The disintegrated fiber is quite dry, and is easily converted into glucose.

The N_2O_3 and SO_2 may be generated by any of the well known processes, but the ordinary methods employed in sulphuric acid making are the most economical. In fact, this process should be operated, possibly, in connection with such works, the gases escaping from the cotton seed chute being absorbed in the tower or conveyed into the leaden chamber, so that there is no loss.

[illegible]

PYRITES AS A MATERIAL FOR THE MANUFACTURE OF SULPHURIC ACID

[illegible]

It is possible by the [illegible] process to treat only low grade ores, and it will surprise most people to learn that the average [illegible] Spanish pyrites rarely exceeds $[illegible] per ton [illegible] $[illegible] per ton [illegible] the [illegible] process [illegible] per cent [illegible] saved [illegible] quantities of [illegible] necessary [illegible]

At [illegible] Works [illegible] simple process [illegible] which [illegible] the settings [illegible] works [illegible]

[illegible] sulphur [illegible] arsenic and [illegible] from [illegible] washed [illegible] is [illegible]

to 1.003 density, until a sample of the solution gives no gold reaction with an acidulated solution of stannic chloride. The solution containing the gold is then heated in wooden tanks by steam to 160 degrees Fahrenheit, and the gold precipitated by means of ferrous sulphate, sodium sulphide, or sulphurous acid, a small quantity of acetate of lead being added during the precipitation to insure the saving of all the gold. The cost of working tailings containing 41.82 grains of gold (about 4 grains left in the residues) was not 25 cents per ton. A richer ore containing 523.62 grains gold per tons (6.02 grains left in the residues) cost only 2.69 per ton for treatment.

In connection with the subject of bricking and roasting certain classes of auriferous sulphides, the attention of metallurgists being now specially directed to this method of handling low-grade ores, it will perhaps be remembered that a very ingenious method was devised by Capt. Crosby, superintendent of the North Barrier gold mine, Cabarrus county, N. C., somewhere about 1867. It consists in the erection of a rectangular kiln, well bound together, and comparable to the old style charcoal furnaces in outside appearance, say 4x10 feet inside measurement, with fireplaces on the ends, and frame doors for the removal of the roast product in the front and rear at the base.

The interior was supposed to be filled with a mixture of sulphurets and clay, made into a brick-like paste in the ordinary pug mill with the admixture of chopped hay or kindred substances. In order to provide draft for the firing, the mass of paste rested upon grate bars, and one-tenth of the interior was taken up by spaces formed by the standing on end of numerous round bars of iron, which were removed when the paste had sufficiently set and as firing progressed.

These ores are crushed to 12 mesh, mixed with 5 to 8 per cent. fresh burned lime, and made into bricks of convenient shape for stacking in an ordinary brick kiln. The entire process then hinges upon careful firing, by which all the sulphides are converted into soluble sulphates, and from this point any of the before-mentioned methods of handling the solutions are applicable in the recovery of the copper, gold and silver. If some portion of the process would yield sulphuretted hydrogen gas cheaply, it

would perhaps be desirable to precipitate the copper etc. by introduction of this gas.

There would then be about a 50 per cent product of copper with formation of free sulphuric acid to be used in subsequent workings.

Still another process of bricking the ores, although by the nature of the gangue the bricks can be made from the ore as it is mined and sorted, is the very successful method pursued in Spain on the Madanpee deposits. The enormous reserves of low grade copper ores, containing not to exceed 1½ per cent, are mined and screened into tram cars for about 5 cents per ton, everything passing a two inch riddle going to Cornish rolls and thence directly to brick machines, the mixture of sulphides and oxides in proper proportion being carefully attended to in order that sufficient sulphuric acid shall be thrown off in the roasting to solubilize the latter. The bricks or slabs are built into kilns in the ordinary way, and allowed to dry for a month before fires are lighted. The roasting occupies three months and is carefully conducted to produce the greatest amount of soluble sulphates.

The lixiviation of this roast, as conducted for the recovery of the copper, iron and precious metals is more than ordinarily interesting, but cannot be dealt with in the limits of this article.

The [illegible] process has been known for several years but has not been generally practised [illegible].

It consists in [illegible] the ore through a [illegible] mesh screen and expose it to [illegible] with a percentage of sulphuric acid [illegible] the sulphuric acid [illegible] expected the [illegible]

[illegible]

[illegible]

hard lumps, and could be used for blast furnace material, or, by a subsequent treatment, fitted for the best grades of paint.

The residues containing gold and silver would be in most convenient shape for treatment by several methods.

The method employed in the large way for treatment of the copper residues in England and continental works, known as the Henderson process, consists in pulverizing the residues from the kilns to pass a twenty-mesh screen, during which operation crude salt is added to the extent of 250 to 300 pounds per ton of cinders. This prepared material is then roasted in a muffle furnace for five hours, the air being excluded until all its copper is known to be soluble in water. An excess of salt present causes the complete solution of the silver, and in some unknown way the gold goes into solution. The roasted charge is cooled, then dumped into vats or tanks which have false bottoms, and leached with a liquor, the product of the fumes from the roasting furnaces caught in coke towers through which water is dripped—a weak hydrochloric acid.

The first three washings of the ore charge are taken off for deposition of the silver and gold by the Claudet process, and the liquor is then run into tanks for the deposition of its contained copper by means of iron.

The simplicity of the plant and perfect control which can be exercised over the necessary operations for conversion of sulphides into soluble chlorides, recommends this process to practical men, and, as the patents have expired, it is now open to use wherever the ores are suitable

During the past few years there have been several practical introductions of electrolytic methods for treatment of ores and mattes, containing gold, silver, copper, etc., their publication by the technical press bringing them to general notice.

A very important innovation on existing methods comes to us lately from the German scientist, Dr. Höpfner, who proposes no less than direct conversion or reduction of copper, silver, etc., from their ores, by means so simple, regular, and inexpensive, as to make available many deposits of minerals at present of no commercial value.

An outline of this process, the fundamental principle of which is the use of chlorides, will prove to observant students how nearly

on parallel lines the great working processes of the past one hundred years have ranged themselves, and how essential to success the minor points, perhaps the baffling part of an almost perfect working, may become when electricity is added to our forces.

Dr Hopfner makes use of a solution of cupric chloride, to which is added in certain definite proportions chlorides of calcium, or sodium. The energetic effect of these solvents is heightened by the action of the electric current, and by simple methods metals are electrolytically deposited, while at the same time a lixivium is produced, which is capable of leaching copper, silver, etc., from raw ores. A cycle is inaugurated by mechanical methods from the depositing to the leaching tanks in manner substantially as follows.

One or more baths are divided by diaphragms into two compartments. One, the anode, contains electrolytic insoluble [illegible] anodes; the other contains copper plate cathodes. A halogen salt cupric chloride solution with chloride of calcium flows by the anode and the cathodes. At the latter [illegible] metallic copper are precipitated by the current unit [illegible] been which is double the quantity heretofore deposited from [illegible] oxide salt solution, for example, copper sulphate solution.

The [illegible] slowly [illegible] past the [illegible] cathode [illegible] from its copper [illegible] being [illegible] use [illegible] copper [illegible] is [illegible] used as [illegible] The [illegible] [illegible] which [illegible] [illegible] from its copper [illegible] that simultan-

eously with the copper, the silver contained in the ores goes into solution, which is not the case when other extraction-liquids are used, for example, ferric sulphate. The silver contained in the lyes is separated by itself, either galvanically,—it detaches itself at the first cathode plates of the first bath,—or chemically before the copper precipitation. The resultant copper is consequently chemically pure. The quantity of copper which can be precipitated in this Höpfner process by a mechanical horse-power = 690 volt amperes, with a pole-tension of 0.8 volt, and with a sufficient number of baths, amounts to 43.9 kilograms (96.58 lbs), the current loss being 10 per cent. Then, as in every ampere hour 2.36 gms. of copper are precipitated, the amount of copper precipitated in a period of twenty-four hours with one volt tension will be

$$\frac{690 \times 2.36 \times 24}{1000 \times 0.8} = 48.8 \text{ kilogrammes } (107.36 \text{ lbs.}).$$

A loss of 10 per cent. deducted from the above calculated quantity of 48.8–4.9 = 43.9 kilogrammes (96.58 lbs.) per horse power per day is given. By the use of larger machinery installations, and by reckoning a fourth of the total work necessary on the requisite pumps and also on the mechanical motion of the lixiviating apparatus, and three-fourths on the electro-dynamic power, it is shown, taking 30 kilogrammes (66 lbs.) of coal per horse power, and 10 per cent. current loss, that almost 33 kilogrammes (72.6 lbs.) of chemically pure copper are obtained from pulverized raw ore with 30 kilogrammes (66 lbs.) of coal. This is a result which has never hitherto been obtained and it finds a use for even the very poorest copper ore. It is clear from the foregoing that the Höpfner process, which is already in application in Saxony, Westphalia, and Norway, is technically worked out to the smallest details, and in all probability it will soon establish for itself a high reputation.

There are numberless suggestions which might be taken from the workings of the trained metallurgists of the world and applied to successful utilization of the ores of the United States.

1st. A railway center is indispensable, contiguous to or within reasonable distance of minerals, such as copper, zinc, lead, etc., with more or less gold and silver.

2d. Coal and coke within easy reach, and at fair average prices.

3d. Markets for products of the works.

4th. Cheap money for carrying the products.

As distinguished from the works now established, such a metallurgical plant would be divided into departments as follows:

First Department. Crushing, sampling and sorting of all ores brought from the several mining sections. Valuations and compositions of all products would here be determined for subsequent operations.

Second Department. Roasting of ores.

a. For manufacture of sulphuric acid direct from gases.

b. In muffle furnaces with tower process for saving [illegible] dric acid from waste gases.

c. In hearth furnaces for regulus.

Third Department. Smelting of all ores which by the [illegible] would properly concentrate to slag or matte by means of heat. T[illegible] regulus from the operations in this department would be [illegible] to the roasting furnaces to be treated for [illegible].

Fourth Department. Chlorination, [illegible] and separation of precious metals [illegible].

Fifth Department. [illegible]

Sixth Department. [illegible]

[illegible]

placed. What would be the result of working mine ores of treble value when the sulphur alone would pay for all costs of extraction? The working cost of the ores mentioned is not greater than $3 per ton, and there are millions of tons of ores in the Southern States which will be worked for less than that sum when Western methods are brought to bear on this problem.

At the Haile mine, in South Carolina, there is a complete plant for the crushing and concentrating of the gold ores found so abundantly on that belt. The concentrates are about 6 per cent. of the stamp stock, and will assay about $35 per ton raw. These concentrates are worked by roasting and chloridizing for about $3.50 per ton, with a result of 95 per cent. assay.

We thus have a basis for calculation (which cannot be confounded with the generalizing so frequently the basis for remarks of this character) which enables us to make the positive statement that sulphuric acid works could be run on this class of material with the following result:

Working statement of a metallurgical process on sulphurets containing gold, by which the sulphuric acid is first saved and the ores then chloridized by the "Thies" method:

Products.

17 tons chamber acid at $10		$170.00
6 tons iron residue at $2		12.00
Gold, 95 per cent. of assay value		332.50
Total value of product		$514.50

Costs.

10 tons of concentrates, from stamps and vanners, charged to works at assay value, $35,	$350.00	
Less loss in treatment, $1.75	17.50	
Net value of concentrates	$332.50	
Less charges for working at $10	100.00	
Net cost of the ore to works	$232.50	
Costs of manufacture of acid, as per cost-sheet in my former article	38.25	
Cost of chloridizing the roasted product to obtain pure gold at $3	30.00	
Total cost on 10 tons concentrate		$300.75
The net profit to the metallurgical works is, daily		$213.75

Or, $21.37½ per ton of ore treated.

Mine engineering and metallurgy are now admitted to be special branches of science requiring closer study and a more intimate knowledge of reactions of the elements in a large way than was possible to compass by the strict old school methods of attaining chemical knowledge alone. The scope is broadening every year and at the same time the field is narrowing as specialists are called to work out problems on so grand a scale. There is room in this country for every variety of talent in special work, but above all and controlling all, there must be the same expansive ideas in management of a metallurgical plant of the character referred to in my remarks as is found in control of each of the successful works already established throughout the country. The business management more than all other things means success or failure to any complicated yet easily divided departmental workings, and whether it be iron, steel, cotton, oil, fertilizers or a metallurgical plant, no mistakes should be made on the score of management; the best man without regard to price should have charge.

It is the earnest wish of many specialists in metallurgy who are well aware of the possibilities of the mining sections of the Atlantic coast that such a works may soon be a reality, and it my writings have had or may have any influence in directing the attention of those most interested to that end, I shall feel that the time has been well spent.

NOTES ON A NEW CRYSTALLINE FERRO-NICKEL ALLOY

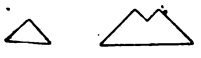
[illegible]

The [illegible] metallurgical [illegible] Mr. [illegible] Mr. H[illegible] Metal[illegible] Nickel [illegible] work [illegible] An alloy [illegible]

In [illegible] the [illegible] of metals [illegible] way to was

lined with brilliant tin-white crystals, which penetrated about half an inch into the surrounding matte. By careful crushing of the matte and separation with a magnet, a few grams of these crystals were obtained sufficiently pure for analysis.

The crystals resembled nothing so much as small corner cuttings of very thin tin-foil, varying in size from a few lines to perhaps half an inch on the longest edge. The form was universally that of a right-angled isosceles triangle, though twinned crystals were often met with.



CRYSTALS OF FERRO-NICKEL.

On examination with a lens no striation or crystalline markings were found on the surface of the crystals, except occasional cubical or square flat crystals of pure copper. The crystals of ferro-nickel were very strongly magnetic, and exceedingly tough and flexible. They were, however, so thin that it was impossible to determine anything in regard to their hardness, it being difficult to see whether the cut made by a knife was due to scratching or shearing by the steel. Owing also to their size and lack of continuity no determination could be made of their tensile strength.

The crystals were either insoluble or very slightly soluble in dilute or strong hydrochloric or sulphuric acid, whether hot or cold, and very slowly soluble in cold dilute nitric acid. In hot dilute nitric acid they were readily soluble, also in aqua regia. In no case was any trace of siliceous or carbonaceous residue noticed after solution of the alloy. Analysis of two selected samples was as follows:

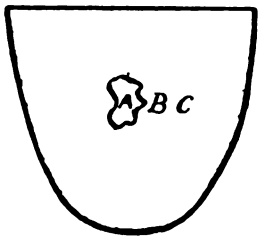
	No. 1.	No. 2.
Copper	4.89	3.64
Iron	43.3	44.0
Nickel	52.1	52.4
	100.29	100.04

Both analyses are a trifle high, owing to the smallness of the samples taken. As is evident from the variation in copper, as well as its crystallizing on the surface of the alloy, copper seems to be a foreign element. Eliminating this, and recalculating analysis of lot No. 2 to 100 per cent., we have:

Iron	45.64
Nickel	54.36
	100.00

This corresponds very nearly to the formula Ni_9Fe_8.

The matte from which these scales separated differed neither in appearance nor method of production from any low grade copper-nickel matte. Analysis of the day's run of matte showed an average of 18.75 per cent. copper and 16.63 per cent. nickel. As a general rule, no variation in percentage of metal is noticed between top and bottom, center or outside of a pot of matte. In this case, however, a segregation of constituents can be seen.



CROSS-SECTION OF A POT OF MATTE SHOWING CAVITY AND LOCATION OF ANALYSES.

A, Scales in cavity at center.
B, matte immediately surrounding scales.
C, matte 6 inches from the scales.

	A.	*B.*	*C.*
Copper	3.64	17.94	19.82
Nickel	52.4	14.50	15.00
Iron	44.0	37.75	36.35
Sulphur	0.0	28.87	27.21

It will be noticed that nickel shows the greatest segregation, that element seeming to withdraw suddenly from the matte at *B* to unite with the iron. Copper appears to have been forced toward the outside of the pot to make room for the inward flow of nickel.

I have very often noticed that a growth of copper crystals will form on the surface of a piece of matte broken when hot, the crystals often forming in a few hours, but I have never before noticed a similar growth of nickel or ferro-nickel crystals. I would be much interested to hear through the columns of this Journal from any chemist of similar phenomena falling under their own observation.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT OF AGRICULTURE, No. XX.]

Read before the Washington Chemical Society, February 11, 1892.
Communicated to this Journal by H. W. Wiley.

THE BEHAVIOUR OF SUGAR SOLUTION WITH ACETONE.

BY WILLIAM H. KRUG AND K. P. MCELROY.

Acetone and water are perfectly miscible in all proportions at ordinary temperatures. If we take such a mixture of acetone and water containing more than 10 per cent. of acetone and add small quantities of sugar, dissolving the latter after each addition, we will reach a point where upon the next addition of sugar the acetone separates out in a clear layer floating on the sugar solution. We can continue to add sugar until the water is saturated. It will then still contain a small percentage of acetone which is soluble even under these conditions. On account of the highly viscous nature of a saturated sugar solution, it is impossible to determine the amount of acetone soluble in it with any accuracy. For 75 degrees C. it is approximately 9.5 per cent.

From the above it is apparent that we can not determine the solubility of sugar in mixtures of acetone and water, but that we must exactly reverse the problem, *i. e.*, determine the solubility of acetone in sugar solutions of varying concentration.

Sucrose is absolutely insoluble in pure acetone. The acetone used boiled at 57.5 degrees C.

The following method was devised for determining the solubility of acetone in sugar solutions:

25 gms. of a sugar solution of known strength were rapidly weighed into a small flask, a small thermometer inserted, and the flask closed with a rubber stopper. The whole apparatus was then weighed. It was brought to the required temperature and acetone added in small quantities from a burette, the flask being stoppered and shaken between each addition. The flask and contents were carefully kept at the required temperature throughout the whole experiment. The first quantities added dissolved quickly, forming a clear liquid. As soon as the point of saturation, however, was reached, the next drop would cause a milkiness, which on standing resolved itself into minute globules of acetone. It was thus very easy to obtain the point of saturation. The flask

was then stoppered and weighed again and the weight of the acetone added found by difference.

As the appended table of duplicate results shows this method was very satisfactory.

The solubility of acetone in sugar solutions decreases as we raise the temperature. Its solubility was determined [illegible] 25 and 30 degrees C., the sugar solutions used ranging from 4[illegible] to 70 per cent. The curves of solubility show that from 4[illegible] to 60 per cent. sugar the lines are practically parallel. From this point to 70 per cent. they approach each other in a regular manner, and it seems probable that in a saturated sugar solution they meet at a common point.

When acetone and water are mixed, heat is evolved, and a diminution of volume similar to that occurring when alcohol and water are mixed, takes place.

Table of Solubility

[illegible] sugar solution [illegible] per cent. [illegible] at

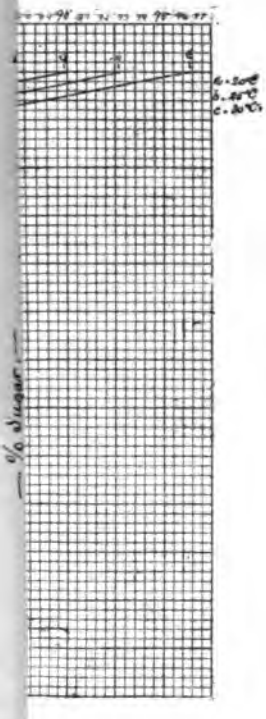
Percent sugar	[illegible] Degrees	[illegible] Degrees	[illegible] Degrees
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

Duplicate Results [illegible] Method [illegible]

[illegible] Degrees

[illegible]			Mean
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]

[illegible] and solubilities of [illegible] acetone



JAS. LEWIS HOWE.

*From advance sheets of the Proceedings of the American Association for the Advancement of Science, Washington Meeting, 1891.

We will continue the study of the [illegible] inorganic and organic compounds with acetone

REPORT OF THE COMMITTEE ON SPELLING AND PRONUNCIATION OF CHEMICAL TERMS.*

During the past four years, your committee has sought to obtain from the members of this Section, from leading American Philologists, and from American Chemists in general, an exhaustive and thoroughly representative expression of opinion on the questions coming within the scope of its commission, which has been essentially the attainment of uniformity in the orthography and pronunciation of the terms used in our science.

Three preliminary reports were distributed to American Chemists in the years 1889, 1890 and 1891, inviting extended criticism and suggestion.

The substance of the replies to these was carefully digested and submitted to the Chemical Section each year for detailed discussion and decision.

The present and final report of your committee embodies the results of these four years of correspondence and discussion, as completed by the sectional action at the present meeting of the Association. It is presented in the hope that all chemists, especially those engaged in teaching, will cordially unite in the effort to bring about the desired uniformity in usage.

The reasons for the adoption of a few more radical changes in our nomenclature are to be found in the report for 1890. Those specially interested in the subject who have not attended the recent sessions of the Association may freely correspond with individual member of the Committee, who will gladly furnish more detailed explanation of the principles involved.

The following summary of rules is not to be regarded as final. Your committee recognize the fact that after a fair trial for a decade or even less, certain modifications will in all probability be generally regarded as desirable.

In conclusion the committee express their sincere thanks to their many colleagues throughout the land, who have so promptly and fully responded to the successive requests for data, suggestions and opinions.

T. H. NORTON,
EDWARD HART,
H. CARRINGTON BOLTON,
JAS. LEWIS HOWE.

*From advance sheets of the Proceedings of the American Association for the Advancement of Science, Washington Meeting, 1891.

Rules for the Orthography and Pronunciation of Chemical Terms

GENERAL PRINCIPLES OF PRONUNCIATION

1. The pronunciation is as much in accord with the analogy of the English language as possible.

2. Derivatives retain as far as possible the accent and pronunciation of the root word.

3. Distinctly chemical compound words retain the accent and pronunciation of each portion.

4. Similarly sounding endings for dissimilar compounds are avoided hence **-id, -ite**.

ACCENT

In polysyllabic chemical words the accent is generally on the antepenult, in words where the vowel of the penult is followed by two consonants, and in all words ending in **-ic** the accent is on the penult.

PREFIXES

All prefixes in strictly chemical words are regarded as parts of compound words, and retain their own pronunciation unchanged as Acetic, Amido, Azo, hydro, iso, nitro, nitroso.

ELEMENTS

In words ending in **-ium**, the vowel of the antepenult is short if **i** is a diphthong or **y** is diphthong or if followed by two consonants as Aluminum, but long otherwise as Titanium, Selenium, Chromium.

aluminum	chromium	iodin	nitrogen
antimony	cobalt	iridium	osmium
arsenic	columbium	iron	oxygen
barium	copper	lithium	palladium

[illegible]

[illegible] N B The accent [illegible] the stress falls but does not [illegible] the word into syllables.

bi'smuth (biz)	dĭdȳ'mium	lead	phŏs'phorus
bō'ron	e'rbium	lĭ'thium	plă'tinum
brō'mĭn	flū'orĭn	magnē'sium	potă'ssium
că'dmium	gă'llium	(zhium)	rhō'dium
că'lcium	germā'nium	ma'nganese	rubĭ'dium
ca'rbon	glū'cinum	(eze)	ruthē'nium
cē'rium	gold	me'rcury	samā'rium
cē'sium	hȳ'drogen	mōlȳ'bdenum	scă'ndium
chlō'rin	ĭ'ndium	nĭ'ckel	sĕlē'nium
sĭ'licon	sŭ'lfur	thō'rium	vănā'dium
silver	tăntalum	tin	ytte'rbium
sō'dium	tellū'rium	tĭtā'nium	ȳ'ttrium
strŏ'ntium	te'rbium	tŭ'ngsten	zinc
(shium)	thă'llium	ūrā'nium	zircō'nium

Also: ămmō'nium, phosphō'nium, hă'logen, cȳă'nogen, ămĭ'dogen.

Note in the above list the spelling of the halogens, cesium and sulfur; **f** is used in the place of **ph** in all derivatives of sulfur (as sulfuric, sulfite, sulfo-, etc.)

TERMINATIONS IN -ic.

The vowel of the penult in polysyllables is short (as cȳă'nic, fūmă'ric, arsĕ'nic, sillĭ'cic, īŏ'dic, būtȳ'ric), except (1) **u** when not before two consonants (as mercū'ric, prŭ'ssic), and (2) when the penult ends in a vowel (as benzō'ic, olē'ic); in dissyllables it is long except before two consonants (as bō'ric, cĭ'tric).

Exceptions: acē'tic or acĕ'tic.

The termination **-ic** is used for metals only where there is a contrast with **-ous** (thus avoid aluminic, ammonic, etc.).

TERMINATIONS IN -ous.

The accent follows the general rule (as plă'tinous, sŭ'lfurous, phŏ'sphorus, coba'ltous). Exception: acē'tous.

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marīne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = ĭ.

' Primary accent; " secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

TERMINATIONS IN -ate and -ite.

The accent follows the general rule (as Ă'cetāte, ă'nalīte); in the following words the accent is thrown back (as Ă'lcohōlāte, Ă'cetonāte, Ă'ntimonite).

TERMINATIONS IN -id (FORMERLY -ide).

The final **e** is dropped in every case and the syllable pronounced **id** (as chlō'rid, i'odid, hy'drid, ō'xid, hydrōx'id, sal'fid, ă'mid, ă'nilid, mūrē'xid).

TERMINATIONS IN -ane, -ene, -ine and -one.

The vowel of these syllables is invariably long (as mē'thane, ē'thane, na'phthalēne, a'nthracēne, prō'pane, gly'nōne, ă'cetōne, kē'tōne).

A few dissyllables have no distinct accent (as benzēne, xylēne, cētēne).

The termination **-ine** is used only in the case of doubly unsaturated hydrocarbons, according to Hermann's grouping.

TERMINATIONS IN -in.

In names of chemical elements and compounds (with the class which includes all those formerly ending in **-ine** except doubly unsaturated hydrocarbons) the final **e** is dropped and the syllable pronounced **-in** (as chlō'rin, bro'min, etc.; ă'min, ă'lkalōid, morphīn, cōdein, ă'nilīn, allōxă'ntin, ălbū'min, emŭ'lsin, cŭ'ttin, cocaīn).

TERMINATIONS IN -ol.

This termination in the [illegible] chemical compounds is used [illegible] and by [illegible] **e**. The [illegible] pronounced **-ol** is [illegible] phenol [illegible] the [illegible] equivalent.

Exceptions [illegible]

[illegible]

[illegible] N.B. The [illegible] stress falls [illegible] syllables.

TERMINATIONS IN -ole.

This termination is always pronounced **-ole**, and its use is limited to compounds, which are not alcohols (as ĭ'ndōle).

TERMINATIONS IN -yl.

No final **e** is used; the syllable is pronounced **yl** (as ă'cetȳl, ă'mȳl, cē'rotȳl, cē'tȳl, ĕ'thȳl).

TERMINATIONS IN -yde.

The **y** is long (as ă'ldehȳde).

TERMINATIONS IN -meter.

The accent follows the general rule (as hydrŏ'meter, barŏ'meter, lactŏ'meter).

Exception: words of this class used in the metric system are regarded as compound words, and each portion retains its own accent (as cĕntime"ter, mi'llime"ter, kĭ'lome"ter).

MISCELLANEOUS WORDS

which do not fall under the preceding rules.

Note the spelling: albumen, albuminous, albumini-ferous, asbestos, gramme, radical.

Note the pronunciation: a'lkalīne, a'lloy (n. & v.) a'llotropy, a'llotropism, ī'somerism, pŏ'lymerism, apparā'tus (sing. & plu.) āqua regia, barȳ'ta, cĕntigrade, co'ncentrated, crystallĭn or crystallīne, electrŏ'lysis, lĭter, mŏ'lecule, mŏlĕ'cular, nō'menclā"ture, olē'fiant, qua'ntivā"lence, vā'lence, ū'nivā"lent, bī'vā"lent, trīvā"lent, qua'drivā"lent, tĭ'trate.

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marīne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = ĭ.

' Primary accent; " secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

A LIST OF WORDS WHOSE USE SHOULD BE AVOIDED IN FAVOR OF THE ACCOMPANYING SYNONYMS.

For	*Use*
beryllium	glucinum
niobium	columbium
thein	caffein
titer (n.)	strength or standard
titer (v.)	titrate
monovalent	univalent
divalent, etc.	bivalent, etc
quantivalence	valence
sodic, calcic, zincic, nickelic, etc., chlorid, etc	sodium, calcium, zinc, nickel, etc., chlorid, etc. and terminations in -ic supra
arsenetted hydrogen	arsin
antimonetted hydrogen	stibin
phosphoretted hydrogen	phosphin
sulfuretted hydrogen, etc.	hydrogen sulfid, etc
alkylogens	alkylhaloids
benzol	benzene
tolnol, etc.	toluene, etc
pyrocatechin	catechol
resorcin	resorcinol
*hydroquinone and hydrochinon	quinol
orcin	orcinol
hydrophlorone	phlorol
phloroglucin	phloroglucol
quercite	quercitol
pinite	pinitol
glycerin	glycerol
erythrite, erythroglucin, eryglucin, erythromannite, phycite	erythrol

[illegible]

[illegible] N B The [illegible] the stress falls [illegible] syllables

[illegible]

mannite	mannitol
dulcite	dulcitol
sorbite	sorbitol
furfurol	furfuraldehyde
fucusol	fucusaldehyde
anisol	methyl phenate
phenetol	ethyl phenate
anethol	methyl allyl-phenol

NOTE.—It has been suggested that the words qualitative and quantitative could be advantageously replaced by qualitive and quantitive, deriving the terms from the Latin adjectives instead of the nouns, as has been done in the case of rotary instead of rotatory, agriculturist instead of agriculturalist, etc. The Section regards this change as eminently desirable, but on account of the extended use of the words outside of chemistry, delays action until the opinions of those in allied branches have been obtained.

Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marīne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = ĭ.

' Primary accent; " secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

XLIII. EXAMINATION OF THE LLOYD METHOD FOR THE ASSAY OF ALKALOIDS.*

BY HERBERT E. SMITH AND THOS. H. NORRIS.

In February, 1891, Prof. J. U. Lloyd read before the Cincinnati Section of the American Chemical Society a paper on the analysis of alkaloids, which was presented later before the American Pharmaceutical Association at its annual meeting (published in pamphlet form) and printed more or less fully in several home and foreign journals. The method proposed, on account of its claims to rapidity and reasonable accuracy, evoked much criticism both friendly and adverse. The possession of a reliable method of placing in the hands of the chemist the means of analyzing easily and quickly the majority of the members of the group of the alkaloids is of such prime importance that we undertook the following study of the process with the view of ascertaining as definitely as possible the limits of accuracy in the case of the leading alkaloids under varying conditions.

The method proposed by Prof. Lloyd, and employed in all our experiments, is, briefly stated, as follows:

[illegible] of an alkaloidal solution are poured into a mortar and a sufficient amount of a mixture of equal parts of tartaric bitartrate and sodium bicarbonate added to form a stiff paste. This magma is then triturated with [illegible] chloroform. Should it seem [illegible] that the magma becomes pulverulent, a small amount of water or [illegible] is added and triturated until a stiff paste is again formed, from which the chloroform separates clearly with [illegible] of turbidity.

The [illegible] extract is decanted into a small porcelain dish and evaporated.

The magma is then washed three times by trituration with [illegible] each time at the wash [illegible] decanted on the same filter.

[illegible] with a 1 per cent solution [illegible] the water [illegible] was the residue [illegible]

The clear solution of the sulfate of the alkaloid, thus obtained, is rendered slightly alkaline by ammonia, and rotated in a separating funnel with 10 cc. of chloroform for about two minutes. This operation is repeated four times, the chloroform being drawn off each time.

The solution of the alkaloid in chloroform is then evaporated to dryness in a small platinum dish or on a watch-glass over the water-bath. While still on the water-bath the residue is stirred with the sharp point of a knife, to ensure the total removal of the chloroform.

After cooling in the desiccator, the dish or watch-glass is weighed with its residue of pure alkaloid.

The chief advantage and essential peculiarity claimed for the process just described is the total avoidance of any emulsion in the chloroform extract from the magma obtained by the treatment with ferric hydrate and sodium bicarbonate at the outset. The remaining steps in the process are practically identical with those hitherto used in similar analytical determinations.

In the study of the method in question, we have extended our experiments over the following subjects, viz:

1. Purity of the chloroform and other reagents used.
2. Insolubility of ammonium sulfate in chloroform.
3. Completeness of the extraction of the alkaloids from the magma.
4. Completeness of the extraction of alkaloids from alkaline solution by rotary agitation with chloroform.
5. Complete assays of pure alkaloids and of their fluid extracts.
6. Increase in weight of certain alkaloids after solution in chloroform and subsequent evaporation.
7. Substitution of aluminum and chromium hydrates for ferric hydrate.
8. Limits of precaution to be observed in weighing.
9. Amounts of moisture present in pure commercial alkaloids.

A. Experimental Part by H. T. Nichols.

I. PURITY OF THE REAGENTS USED.

Chloroform.—The purity of the chloroform used should be tested by evaporating about 10 cc. on the water-bath. If pure enough for the purpose in view, it should leave absolutely no residue.

This precautionary test is especially necessary in the case of chloroform which is not of recent manufacture. Where many determinations of this nature are made, a large proportion of the chloroform can be saved by evaporation beneath an inverted funnel leading to a condenser through which a current of air is drawn. If rubber connections are used redistillation is of course necessary.

Ferric hydrate and calcium hydrate. These should be free or at least free from all substances capable of being dissolved by chloroform.

The reagents used in the following analyses were treated with 5% chloroform and the decanted liquor left no residue.

II. INSOLUBILITY OF AMMONIUM SULFATE IN CHLOROFORM.

As no statements with regard to the solvent powers of chloroform on ammonium sulfate are on record it seemed desirable to decide the question by actual experiment.

Several grams of ammonium sulfate were triturated with [illegible] of chloroform and filtered. The filtrate evaporated [illegible] the water both left no weighable residue. This experiment was repeated two times with the same result.

[illegible] 5 per cent solution of sulfuric acid were [illegible] with [illegible] times. The chloroform was then drawn off and evaporated to dryness on the water bath. There was a slight residue [illegible] was without burning to ash.

[illegible]

[illegible]

[illegible]

This observation was confirmed by three experiments in which solutions of ammonium acetate were evaporated to dryness, and left no residue.

III. COMPLETENESS OF THE EXTRACTION OF ALKALOIDS FROM THE MAGMA BY CHLOROFORM.

Three series of tests were made to ascertain whether any appreciable amount of alkaloid remained in the magma after four extractions with chloroform.

Several magmas containing nux vomica were extracted in the usual manner.

In no case was the intensely bitter taste peculiar to this alkaloid perceptible after the third washing with chloroform.

A weighed amount of cinchonin, one part of which is soluble in over three hundred parts of chloroform, was treated as before.

The residue obtained from the chloroform extract was almost equal to the amount used, showing that even in the case of this difficultly soluble alkaloid, scarcely any portion was retained by the magma.

A further test of the delicacy of the process was shown by the following experiment:

0.00001 gm. of a mixture of brucin and strychnin was put through the assay and the residue on the watch-glass, though not visible, still yielded the bitter taste of the alkaloids.

IV. COMPLETENESS OF THE EXTRACTION OF ALKALOIDS FROM ALKALINE SOLUTIONS BY ROTARY AGITATION WITH CHLOROFORM.

Experiments were made to find the number of rotations necessary for the complete extraction of an alkaloid when the solution of the alkaloid and ammonium sulfate is rotated with chloroform. 1 gm. of an alkaloid was dissolved in acidulated water, and the solution was made up to 100 cc. or a 1 per cent. solution. 10 cc. of this solution were used each time, containing in each case, therefore, 0.1 gm.

Each portion was rendered slightly alkaline by the addition of ammonia, put into a separating funnel, and rotated with chloroform. The dried residue obtained from the chloroform drawn off after each period of rotation was weighed separately.

The rotations were made with the circling motion suggested in his article by Prof. Lloyd, and precautions were observed to pre-

vent the liquids from being shaken together. The average time of each period of rotation was about two minutes.

Caffein. Amount used, [illegible] gm.

[illegible]

	First Rotation	Second Rotation	Third Rotation	Fourth Rotation	Total Amount Lost
A	[illegible] gm	[illegible] gm	[illegible] gm	[illegible] gm	[illegible] gm
B	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
D	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
E	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

The greatest loss occurred in *E*, [illegible] gm. The least loss was in *C*, [illegible] gm. The average loss was [illegible] gm, or [illegible] per cent.

Brucin. Amount used, [illegible] gm.

[illegible]

	First Rotation	Second Rotation	Third Rotation	Total Amount Lost
A	[illegible] gm	[illegible] gm	[illegible] gm	[illegible] gm
B	[illegible]	[illegible]	[illegible]	[illegible]
C	[illegible]	[illegible]	[illegible]	[illegible]
D	[illegible]	[illegible]	[illegible]	[illegible]
E	[illegible]	[illegible]	[illegible]	[illegible]
Average	[illegible]	[illegible]	[illegible]	[illegible]

Average total gain, [illegible] per cent.

[illegible]

It will be noticed that the total amount has increased [illegible] original amount, [illegible] per cent [illegible] on average. As will be seen later on, the cause of the increase in weight of cotton [illegible] after treatment with chloroform, this result was to be expected.

[illegible]

[illegible]

A	[illegible]	[illegible]	[illegible] gm	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

Atropin.—Amount used, .1 gm.

Amount Recovered after each Successive Rotation.

	First Rotation.	Second Rotation.	Third Rotation.	Total Amount Recovered.
A . . .	.0926 gm.	.0032 gm.	.0000 gm.	.0958 gm.
B	.0786 "	.0116 "	.0032 "	.0934 "
C	.0928 "	.0024 "	.0000 "	.0952 "
D	.0916 "	.0030 "	.0000 "	.0946 "
E	.0890 "	.0062 "	.0010 "	.0952 "
Average,	.0889 "	.0053 "	.0008 "	.0948 "

Average total loss, 5.2 per cent.

The variations in total loss ranged from 4.2 to 6.6 per cent.

Aconitin.—Amount used, .1 gm.

Amount Recovered after each Successive Rotation.

	First Rotation.	Second Rotation.	Third Rotation.	Total Amount Recovered.
A	.0960 gm.	.0040 gm.	.0006 gm.	.1006 gm.
B	.1066 "	.0042 "	.0002 "	.1110 "
C	.0998 "	.0036 "	.0004 "	.1038 "
D	.0926 "	.0036 "	.0002 "	.0964 "
E	.0923 "	.0030 "	.0000 "	.0966 "
Average,	.0977 "	.0037 "	.0003 "	.1017 "

Average total gain, 1.7 per cent.

The variations in the total loss or gain ranged from 3.6 per cent. loss to 11 per cent. gain. The latter high figure, obtained in but instance, is to be considered as probably due to error.

Quinin.—Amount used, .1 gm.

Amount Recovered after each Successive Rotation.

	First Rotation.	Second Rotation.	Third Rotation.	Total Amount Recovered.
A	.0996 gm.	.0052 gm.	.0000 gm.	.1048 gm.
B	.0974 "	.0022 "	.0002 "	.0998 "
C	.0990 "	.0026 "	.0002 "	.1018 "
D	.0966 "	.0040 "	.0006 "	.1012 "
E	.0954 "	.0020 "	.0000 "	.0974 "
Average,	.0976 "	.0032 "	.0002 "	.1010 "

Average total gain, 1.2 per cent.

The variations in the total loss or gain ranged from 2.6 per cent. loss to 4.8 per cent. gain.

Cinchonin.—Amount used, [illegible] gm

[illegible]

	First Rotation	Second Rotation	Third Rotation	Total Average Rotation
A	[illegible] gm	[illegible] gm	[illegible] gm	[illegible] gm
B	[illegible]	[illegible]	[illegible]	[illegible]
C	[illegible]	[illegible]	[illegible]	[illegible]
D	[illegible]	[illegible]	[illegible]	[illegible]
E	[illegible]	[illegible]	[illegible]	[illegible]
Average	[illegible]	[illegible]	[illegible]	[illegible]

Average total loss [illegible] per cent

The variations in the total loss ranged from [illegible] per cent

Cincomin is soluble with difficulty in chloroform and therefore the amount of alkaloid obtained in the first rotation is less than in the case of other alkaloids

Cinchonidin—Amount used, [illegible] gm

[illegible]

	First Rotation	Second Rotation	Third Rotation	Total Average Rotation
A	[illegible] gm	[illegible] gm	[illegible] gm	[illegible] gm
B	[illegible]	[illegible]	[illegible]	[illegible]
C	[illegible]	[illegible]	[illegible]	[illegible]
D	[illegible]	[illegible]	[illegible]	[illegible]
E	[illegible]	[illegible]	[illegible]	[illegible]
Average	[illegible]	[illegible]	[illegible]	[illegible]

Average total loss [illegible] per cent

The variations in the total loss ranged from [illegible] per cent

SUMMARY

The highest average gain was in the case of brucin, amounting to [illegible] per cent, and the lowest average gain was in the case of quinin, amounting to [illegible] per cent. The lowest average loss was in the case of cinchonin, amounting to [illegible] per cent, and the highest average loss was in the case of strychnin, amounting to [illegible] per cent. [illegible] in but few instances was [illegible]

[illegible]

[illegible]

Fluid extracts are alcoholic or hydro-alcoholic solutions of the soluble constituents of vegetable products, those of alkaloidal drugs containing the alkaloids in natural combination.

To test the method most thoroughly, parallel determinations were made, first of a fluid extract, next of the same fluid extract with a known amount of its proper alkaloid added, and thirdly of a standard solution of the alkaloid dissolved in alcohol and water.

In this manner the fluid extracts and alkaloids of nux vomica, belladonna, guarana, ipecac, aconite root, and henbane were assayed. The fluid extracts used were those obtained in commerce.

Nux Vomica.—Five samples of the same fluid extract were analyzed:

Percentages Obtained.					
I.	II.	III.	IV.	V.	Average.
1.39%	1.50%	1.45%	1.46%	1.39%	1.44%

.125 gm. of strychnin and .125 gm. of brucin were added to 50 cc. of the fluid extract, and 5 cc. were used in each assay. The results were as follows:

Percentages Obtained.						
I.	II.	III.	IV.	V.	Average.	Theory.
2.03%	1.98%	1.95%	2.00%	2.00%	1.99%	1.94%

The increase in amount is due to the property shown by brucin of increasing in weight after treatment with chloroform. See paragraph VI.

.75 gm. of the mixture of pure brucin and strychnin was dissolved in 50 cc. of alcohol and water, making a 1.5 per cent. solution.

The results of the analysis were as follows:

Percentages Obtained.						
I.	II.	III.	IV.	V.	Average.	Amount Used.
1.60%	1.51%	1.48%	1.47%	1.52%	1.52%	1.50%

Average increase, .02 per cent., or 1.3 per cent. of the alkaloid used.

Belladonna.—The fluid extract of belladonna was assayed with the following results, all from the same sample:

Percentages Obtained.					
I.	II.	III.	IV.	V.	Average.
0.50%	0.55%	0.54%	0.52%	0.50%	0.52%

The greatest variation from the average was .03 per cent., or 6 per cent. of the weight of the alkaloid.

To 100 cc. of the same sample of fluid extract, 1 gm. of pure atropin was added, and the following results were obtained:

[illegible]

I	II	III	IV	V	Average	[illegible]
1.49%	1.46%	1.46%	1.49%	1.52%	1.48	1.52

In analyzing the pure alkaloid, it was found that a solution of atropin in alcohol and water deteriorated so rapidly that the same solution could not be used for comparative assays. The [illegible] was therefore weighed directly each time. The results were as follows:

[illegible]

I	II	III	IV	V
1.12	1.2[illegible]	1.4[illegible]	1.3[illegible]	[illegible]

[illegible]

I	II	III	IV	
1.4[illegible]	1.35	1.4[illegible]	1.4[illegible]	[illegible]

Guarana.—The fluid extract of guarana can be analyzed [illegible] rect determination from the chloroform extract obtained from the magma. The results were as follows:

I	II	III	IV	V	Average
3.84	3.8[illegible]	3.84	3.7[illegible]	[illegible]	[illegible]

1 gm. of caffein was dissolved in [illegible] of the fluid extract of guarana, and the strengthened extract was assayed with the following results:

I	II	III	IV	V	Average	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible] were dissolved [illegible] alcohol and water [illegible] which was analyzed as follows:

I	[illegible]	[illegible]	V	Average	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible] which results

[illegible]	[illegible]	[illegible]	Average
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible] and unstable nature

that it was considered useless to carry out the check experiments employed in the cases of the preceding alkaloids.

Aconite Root.—The assays of the fluid extract of aconite root gave the following results:

I.	II.	III.	IV.	V.	Average.
0.41%	0.42%	0.41%	0.44%	0.42%	0.42%

In these analyses the greatest variation is 5 per cent. of the alkaloid present.

It was not deemed expedient to make experiments with alkaloidal addition to the fluid extract of aconite root or of hyoscyamus, on account of the instability of aconitin and hyoscyamin.

Hyoscyamus.—The fluid extract of hyoscyamus was assayed as follows:

I.	II.	III.	IV.	V.	Average.
0.10%	0.10%	0.09%	0.09%	0.10%	0.10%

VI. INCREASE IN WEIGHT OF CERTAIN ALKALOIDS AFTER SOLUTION IN CHLOROFORM AND SUBSEQUENT EVAPORATION.

An interesting and important fact noticed in connection with this work was the alteration in weight of some alkaloids after solution in chloroform, and subsequent evaporation. This alteration, usually a gain in weight, was most noticeable in the case of brucin.

The real nature of this change was not ascertained. As, however, it has a marked bearing on the value of the process in question, a series of experiments as to the extent of this variation was carried out in the following manner.

A weighed amount of an alkaloid varying from 0.1 to 0.01 gm. was dissolved in chloroform, the solution placed upon a tared watch-glass, and then evaporated on the water-bath to dryness. In the case of those alkaloids which were left in a gummy condition, the residues were stirred with the point of a pen-knife.

The glass was then cooled in a desiccator, over calcium chlorid, for about ten minutes, and quickly weighed.

Caffein.—Caffein, unlike most alkaloids, leaves a crystalline residue. The variations noted were inconsiderable, except where small amounts were used.

The figures obtained were as follows:

Amount of Caffein Used	I	II	III	IV	V	Average
0.1 gm	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0.05 "	[illegible]	2.9	[illegible]	[illegible]	2.1	[illegible]
0.01 "	[illegible]	[illegible]	3.0	[illegible]	11	[illegible]

Brucin.—The results obtained were as follows:

Amount of Brucin Used	I	II	III	IV	V	Average
0.1 gm	6.6	9.3	9.8	9.4	[illegible]	[illegible]
0.05 "	8.3	6.6	6.3	9.8	11	[illegible]
0.01 "	6.3	3.2	4.4	[illegible]	4.9	[illegible]

Average [illegible]

It will be noticed that the range of variation increases as the amount of the alkaloid used in the evaporation decreases.

Strychnin.—The results obtained were as follows:

Amount of Strychnin Used	I	II	III	IV	V	Average
0.1 gm	[illegible]	6.8	4.7	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]

Average [illegible]

Atropin.—The results obtained were as follows:

Amount of Atropin Used	I	II	III	IV	V	Average
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Average [illegible]

Morphin.—The results obtained were as follows:

Amount of Morphin Used	I	II	III	IV	V	Average
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]			[illegible]	
		[illegible]	[illegible]			[illegible]

Average [illegible]

[illegible]

Quinin.—The results obtained were as follows:

Amount of Quinin Used.	Percentages of Loss or Gain. I.	II.	III.	IV.	V.	Average.
0.1 gm. . . .	0.4%	—0.2%	1.1%	3.4%	1.3%	1.2%
0.05 " . . .	—0.7	0.0	7.1	0.0	1.5	1.6
0.01 " . . .	0.0	0.0	1.9	0.0	3.3	1.0
						Average, 1.3%

The average gain is comparatively slight, although the variations range from —0.7 per cent. to +7.1 per cent.

Cinchonin.—The results obtained were as follows:

Amount of Cinchonin Used.	Percentages of Loss or Gain. I.	II.	III.	IV.	V.	Average.
0.1 gm. . . .	0.0%	0.0%	—0.5%	0.0%	0.0%	—0.1%
0.05 " . . .	0.7	1.9	1.7	0.0	1.9	1.2
0.01 " . . .	0.0	0.0	0.0	0.0	—2.0	—0.4
						Average, 0.1%

Cinchonidin.—The results obtained were as follows:

Amount of Cinchonidin Used.	Percentages of Gain. I.	II.	III.	IV.	V.	Average.
0.1 gm. . .	0.0%	0.4%	0.4%	0.0%	0.2%	0.2%
0.05 " . . .	0.0	0.4	0.4	1.1	1.9	0.7
0.01 " . . .	7.9	2.2	0.0	0.0	5.7	3.1
						Average, 1.3%

VII. SUBSTITUTION OF ALUMINUM OR CHROMIUM HYDRATES FOR FERRIC HYDRATE.

Experiments were made with both of these substances to test their availability as reagents in this process, and it was found that if for any reason it is desirable to avoid the presence of iron, either aluminum or chromium hydrate can easily be used as a substitute, both making a good magma and rendering the tannate insoluble. Neither of these substances offers any especial advantage, however, over the ferric hydrate, which is also preferable on account of its cheapness.

VIII. LIMITS OF NECESSARY PRECAUTION IN WEIGHING.

In order to note the difference in weight between cooling in a desiccator and in the open air, several fluid extracts were assayed;

the residues obtained at 100° on a tared watch-glass were cooled in a desiccator, and weighed. They were then reheated and cooled for twenty minutes in the open air, and again weighed. Again the same residues were heated and cooled for one hour in the air and weighed. The results were as follows:

Nux vomica, cooled in the desiccator		[illegible] per cent
" "	20 minutes in the air	[illegible]
" "	1 hour in the air	[illegible]
Belladonna	in the desiccator	[illegible]
" "	20 minutes in the air	[illegible]
" "	1 hour in the air	[illegible]
Aconite root	in the desiccator	[illegible]
	20 minutes in the air	[illegible]
"	1 hour in the air	[illegible]

The alkaloids of ipecac and henbane seemed to be more or less decomposed by reheating.

IN MOISTURE IN VARIOUS COMMERCIAL ALKALOIDS

The pure alkaloids used in the preceding experiments bore the labels of reputable manufacturers, and were found to contain variable amounts of moisture, which were either removed or allowed for in the calculation.

These amounts were as follows:

[illegible]	[illegible] per cent
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

[illegible] SUMMARY OF RESULTS IN THE NORTON

The [illegible] method for the [illegible] determination [illegible] such that I have [illegible] with [illegible] the preceding pages. The [illegible] expected to [illegible] [illegible] [illegible] results [illegible] of impurities [illegible]

counted upon when the process is employed by those less familiar with chemical manipulation, as in the case of the average pharmacist or physician. All results obtained were recorded in order to afford a correct average representation of the working of the method, and this fact will explain the presence of a few abnormal deviations in certain series, which would naturally be eliminated from consideration in establishing averages.

The data here given afford valuable material for estimating the accuracy of the process as one worthy of being incorporated among our standard methods of analysis, and for defining the limitations of its useful application. Its widest field would naturally be in the analysis of alkaloidal preparations for medicinal use, as well as in the assay of crude drugs, and these data may, therefore, be useful to those engaged upon the revision of the National Pharmacopoeia. Any recommendation in this direction would scarcely be in place here.

With regard to the applicability of the method, it is to be noted that it does not aim to separate one alkaloid from another, that its sole purpose is to determine gravimetrically the amount of non-volatile alkaloid or alkaloids, soluble in chloroform (or ether) present in a drug or solution, such as a fluid extract. In passing judgment upon the utility of the method, it is further necessary to bear in mind the varying tendencies of the alkaloids to undergo decomposition. Time, light, temperature, the nature of solvents, all are factors in producing more or less deterioration in the great majority of members of this class.

Keeping these facts in view, the results of this investigation may be briefly summarized as follows:

1. The manipulation involved in the method is exceedingly simple, and fairly uniform results should be obtained by one familiar with elementary quantitative work.

2. Absolutely pure chloroform must be used. The three hydroxides, $Fe_2(OH)_6$, $Cr_2(OH)_6$ and $Al_2(OH)_6$, may be used indifferently in the production of a magma.

3. Ammonium sulfate is totally insoluble in chloroform.

4. The completeness of the extraction of alkaloids from the ferric magma by means of chloroform is all that the most rigid analyst can demand. This was proved gravimetrically in the case of

the difficultly soluble cinchonin, and by means of the [illegible] taste with emetin, brucin and strychnin.

5. The extraction of alkaloids from an alkaline solution in the presence of ammonium sulfate, by means of chloroform [illegible] plete after three treatments, and very nearly so after two [illegible] cases of brucin, strychnin, atropin, aconitin, quinin [illegible] and cinchonidin, while an additional treatment is necessary [illegible] case of caffein.

6. The recovery of alkaloids under the conditions given in the above paragraph is somewhat variable, as will be seen from the table summarizing the losses and gains and arranged according to the range of variation, beginning with the least variable.

[illegible]

Alkaloid	Lowest	Highest	Average
Atropin	[illegible]	[illegible]	[illegible]
Caffein	[illegible]	[illegible]	[illegible]
Quinin	[illegible]	[illegible]	
Aconitin*	[illegible]	[illegible]	[illegible]
Cinchonin	[illegible]	[illegible]	[illegible]
Cinchonidin	[illegible]	[illegible]	[illegible]
Brucin*	[illegible]	[illegible]	[illegible]
Strychnin	[illegible]	[illegible]	[illegible]

In several cases, as in those of brucin, aconitin and [illegible] increase is due to the treatment with chloroform as [illegible] plained in paragraph 7. In all other instances there is more or less loss, compensated by variation in the results, ranging from [illegible] per cent in the case of atropin to [illegible] per cent in the case of brucin.

It is evident that the best element of uncertainty in the [illegible] the method [illegible] at this stage. The difficulties [illegible] the alkaloids [illegible] been [illegible] process of their determination [illegible] extent [illegible] further [illegible]

[illegible]

Amounts Recovered from 100 parts in a Series of Five Analyses, in each of which 0.1 gm. was used.

Alkaloid Used.	Lowest.	Highest.	Average.
Atropin	100.2	102.2	100.6
Caffeïn	99.2	100.0	99.7
Quinin	99.8	103.4	101.2
Aconitin	104.1	106.7	105.5
Cinchonin	99.5	100.0	99.1
Cinchonidin	100.0	100.4	100.2
Brucin	106.6	109.8	108.9
Strychnin	93.5	102.7	98.2

Strychnin exhibits great variation with a tendency to loss. Caffeïn, cinchonin and cinchonidin, are apparently unaltered. Atropin and quinin gain slightly in weight, aconitin more so, and brucin most of all. The range of variation, except in the case of strychnin, is much more limited than in the preceding table. This increase of weight, as the result of treatment with chloroform, is an interesting and important fact, and a more extended study of its real nature is reserved for a later paper. The results summarized in this paragraph, applied as a correction to those given in paragraph 6, show the following average deterioration of the alkaloids, due to the first stages of the process, viz., from the formation of the magma to the final extraction with chloroform :

	Deterioration.
Atropin	5.8 per cent.
Caffeïn	4.4 "
Quinin	0.2 "
Aconitin	5.3 "
Cinchonin	7.2 "
Cinchonidin	5.3 "
Brucin	.7 " gain.
Strychnin	7.6 "

It will be seen that quinin and brucin are the two alkaloids in the list, least liable to decomposition, while the average deterioration of the other six alkaloids ranges from 4.4 per cent. to 7.6 per cent.

8. The results obtained by the direct analysis of fluid extracts are tabulated as follows, and show the degree of uniformity to be expected in the application of the method to several of the ordinary alkaloidal solutions of commerce :

[illegible]

Alkaloids in Extract	[illegible]	[illegible]	[illegible]
Nux vomica	[illegible]	[illegible]	[illegible]
Belladonna	[illegible]	[illegible]	
Guarana	[illegible]	[illegible]	[illegible]
Aconite	[illegible]	[illegible]	[illegible]
Hyoscyamus	[illegible]	[illegible]	[illegible]
Ipecac	[illegible]	[illegible]	[illegible]

Three of these same solutions remoistened with [illegible] known amounts of the corresponding alkaloids in the pure state gave the following results

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Nux vomica plus a mixture of equal amounts of brucine and strychnine	[illegible]	[illegible]	[illegible]	[illegible]
Belladonna plus atropine	[illegible]	[illegible]	[illegible]	[illegible]
Guarana plus caffeine	[illegible]	[illegible]	[illegible]	[illegible]

Analyses of the pure alkaloids used to remoisten the [illegible] extracts gave the following results

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Equal amounts of brucine and strychnine	[illegible]	[illegible]	[illegible]	[illegible]
Caffeine	[illegible]	[illegible]	[illegible]	[illegible]
Atropine	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

XLIV. APPLICATION OF THE PEARSON METHOD OF DETERMINING SULFUR TO THE ANALYSIS OF HORN.

By T. H. Norton and I. J. Smith.

The accuracy of Pearson's method of sulfur determination, based upon oxidation with nitric acid and potassium chlorate as applied to the analysis of sulfonates and derivatives of sulfonic acids, was shown a few years since by Norton and Otten.* Having occasion recently to analyze various samples of horn, it seemed desirable to determine the applicability of the method to the determination of sulfur in this substance, which may well be taken as a type of the natural organic compounds in which the element occurs.

The course of analysis was identical with that described in the above papers. Check analyses were made by the method of Rivot, Beudant and Daguin†, in which the oxidation is effected by passing a current of chlorin through the hot solution of the sulfur compound in potash.

The following results were obtained:

Sample I.

1. 0.7949 gm. of horn shavings gave by Pearson's method 0.2002 gm. of $BaSO_4$ = 0.0274 gm. of S, or 3.46 per cent.
2. 0.5616 gm. gave, by the same method, 0.1333 gm. of $BaSO_4$, = 0.0183 gm. of S, or 3.25 per cent.
3. 2.2892 gm. gave by Rivot's method 0.5598 gm. of $BaSO_4$ = 0.0769 gm. of S., or 3.36 per cent.
4. 1.1428 gm. gave, by the same method, 0.28 gm. of $BaSO_4$ = 0.0384 gm. of S, or 3.36 per cent.

Sample II.

1. 0.5226 gm. of horn shavings gave by Pearson's method 0.144 gm. of $BaSO_4$ = 0.0197 gm. of S, or 3.75 per cent.
2. 0.461 gm. gave by the same method 0.1338 gm. of $BaSO_4$ = 0.0183 gm. of S, or 3.98 per cent.
3. 0.5 gm. gave by Rivot's method 0.147 gm. of $BaSO_4$ = 0.019 gm. of S, or 3.83 per cent.

Summary.

By Pearson's Method.	*By Rivot's Method.*
SAMPLE I.	
1. 3.46 per cent.	1. 3.36 per cent.
2. 3.25 "	2. 3.36 "
SAMPLE II.	
1. 3.75 per cent.	1. 3.83 per cent.
2. 3.98 "	

*Am. Chem. Jour. **10**, 130, 141.
†Comptes rendus de l'Academie des Sciences, 1853, p. 835.

While both methods give satisfactory results Pearson [illegible] questionably the preferable It involves less time and less [illegible] diture of heat, while it totally does away with the [illegible] resulting from the use of a current of chloroform

[illegible] March [illegible]

NEW BOOKS

Tillman's Lessons in Heat. This book is just what it [illegible] tends to be, an elementary treatise on heat It gives all [illegible] tion necessary for the general student without lengthy des[illegible] of apparatus and experiment It is brought up to date [illegible] tains accounts of the recent observations of Prof Langley [illegible] waves and their absorption by the atmosphere [illegible] given of Prof Ferrell's mathematical investigations [illegible] modern theories of cyclones and tornadoes [illegible] theories of the deposition of dew

The author in treating of the normal pressure of the atmosphere quotes the well known theoretical conclusions [illegible] Prof William Ferrel in his able treatise on this subject [illegible] marks that these conclusions were confirmed by observations published in [illegible] which proved the [illegible] pressure [illegible] The [illegible] must have [illegible] the [illegible] [illegible] Prof James H [illegible] [illegible] the Northern Hemisphere [illegible]

[illegible] Washington [illegible] Dr [illegible] Washington [illegible] Ross [illegible] Society [illegible] [illegible] pressure [illegible] [illegible] Prof [illegible] [illegible]

[illegible]

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DETERMINATION OF COPPER AND NICKEL IN ORES AND FURNACE PRODUCTS.

BY DAVID H. BROWNE.

The following scheme for analysis of copper nickel ores, mattes and slags is presented, not with any claim to novelty or originality, but merely as a guide to practical laboratory routine. The chemical principles embodied are all taken from Fresenius and Classen, and the arrangement of work in regard to time is the method found best suited to the daily work of the Laboratory of the Canadian Copper Co. at Sudbury, Ontario.

Of green and roasted ores, as well as slags and other furnace products, with not over 10 per cent. combined metals, 1 gm. of finely pulverized sample is weighed in a No. 1 Griffin beaker. All work is done in duplicate; the two samples being numbered with consecutive analysis number, viz., 1623A and 1623B. Of ordinary smelter mattes averaging 40 to 50 per cent. metal, half a gram is weighed; while of refined matte or metallic samples, a quarter gram is found sufficient.

The samples, some half dozen to each operator, are weighed, if possible, in time to start the determination of copper about five o'clock. As the time taken by the analysis is an interesting factor, I have here made a chart showing this relation.

Monday, 3 P. M. Weigh a half dozen ore samples; dissolve in about 10 cc. strong HNO_3 and 3 cc. HCl; evaporate slowly to dryness.

Monday, 5 P. M. Dissolve in H_2O and a few drops H_2SO_4, filter; add a drop or two strong HNO_3, place in a tall 7 oz. beaker, put on battery with platinum foil in the form of a cylinder 2½ inches long and 1 inch diameter as cathode, and a platinum wire in form of a corkscrew inside this as an anode. Connect with very gentle current, four gravity cells being usually sufficient for six copper solutions. Leave on over night.

Tuesday, 8 A. M. Take off platinums on which copper is precipitated. These are previously tested by passing H_2S into a few cc. of the [illegible] in a small beaker to prove copper is all precipitated. Copper shows as a firm crystalline plating of rose pink color and very [illegible] sponge at ends of cylinder. It is difficult to prevent sponging when the percentage of copper is high, but careful attention to the strength of the current will reduce this trouble to a minimum. Coppers are washed with alcohol and weighed. The solution is evaporated with HNO_3 and heat; the iron is precipitated by two ammonia precipitations; the filtrates are united in a No. 6 Gooch's beaker and concentrated on sand bath. This takes till about 1 A. M. for six solutions.

Tuesday, 10 A. M. The ferric hydrate of second ammonia precipitation is dissolved in HCl in a flask holding about [illegible] is neutralized with Na_2CO_3 solution, the carbonate being added in a burette towards the end to secure a neutral point. [illegible] are then poured in a teaspoonful of crystallized Na_2HPO_4 [illegible] the flask placed under the tap and half filled with [illegible]. The flask is placed over lamp and just brought to [illegible]. A rinsing motion which assists the ferric hydrate to settle [illegible] into a No. [illegible] beaker through a filter. No. [illegible] through two No. [illegible] papers. The flask is rinsed out with [illegible] the nitrate placed on the sand bath over the [illegible].

Tuesday, 1 P. M. The nitrates are now evaporated [illegible] [illegible]

[illegible]

[illegible]

Wednesday, 8 A. M. The nickels should be precipitated, leaving solutions with no blue color, and still strongly ammoniacal. The coppers also which are put on every afternoon are supposed to be ready to weigh at the same time as the nickels.

The above outline will show that accuracy is much more of a desideratum than rapidity. By reducing the work to a systematic routine, any clever workman who can read and follow directions, can make as good a separation of nickel from copper and iron as the most skillful analyst. The accuracy of the above method will be seen from comparing our analysis of a shipment of low grade matte with that of one of the best known New York analysts whom I will call D.

	Copper.	Nickel.
Our analysis averaged . . .	22.92 per cent.	17.60 per cent.
D's " " . . .	22.99 "	17.665 "

The samples were taken separately, ours from the cars here as the shipment was loaded, and D's sample in New York. Another example of triplicate analyses made by us of a low grade matte shows similar agreement.

	Copper.	Nickel.
A	18.72 per cent.	16.10 per cent.
B	18.70 "	16.10 "
C	18.71 "	16.10 "

If we wish to save time, one sample is taken and duplicate electrolytic determinations made of copper; while in two other samples the copper is precipitated from an hydrochloric acid solution by sulphuretted hydrogen, and the filtrate treated as above for nickel.

At the other furnaces in the Sudbury district, the English cyanide method is used both for copper and nickel. The potassium cyanide method for copper is too well known to need description; but an outline of the method for nickel may be of interest.

A much larger quantity of ore or matte is taken for analysis than is customary where the electrolytic method is in vogue. The substance is dissolved as usual; copper is precipitated by sulphuretted hydrogen; iron is removed by one basic acetate separation; nickel is precipitated in ammoniacal solution by sulphuretted hydrogen, and is filtered and burned as above. The residue is dis-

solved in aqua regia or nitric acid, then neutralized by [illegible]. This precipitates some iron, which may carry a little [illegible]. This is filtered, redissolved in hydrochloric [illegible] and the filtrates are united. The solution of nickel [illegible] acid and is titrated by a strong solution of potassium [illegible] which is run in from a burette till the first permanent precipitate of nickel cyanide is redissolved. The solution of potassium [illegible] is made up by dissolving a pound of potassium [illegible] gallon acid bottle of distilled water and should be standardized about every week with pure nickel.

I have not found this method satisfactory, as a very small amount of acid is sufficient to destroy the sharpness of the final reaction. As a rapid and approximate method of estimating the amount of nickel in an ore or matte it may be of some [illegible]; as an accurate method of determination of the exact percentage of nickel, the electrolytic method cannot at present be superseded.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. [illegible]

THE SOLUBILITY OF VARIOUS INORGANIC SALTS IN ACETONE AND OF ACETONE IN DILUTE SOLUTIONS

[illegible]

We have investigated the solubility of some inorganic salts in acetone, the results being given in the following table.

[illegible]

Bromides.

Potassium bromide	slightly soluble.
Sodium bromide	slightly soluble.
Cadmium bromide (anhydrous)	freely soluble.

Iodides.

Potassium iodide	soluble.
Mercuric iodide	soluble.

Cyanides and Sulphocyanides.

Mercuric cyanide	freely soluble.
Potassium sulphocyanide	freely soluble.
Ammonium sulphocyanide	freely soluble.
Ferric sulphocyanide	soluble.
Cobaltous sulphocyanide	soluble.
Nickelous sulphocyanide	insoluble.

Nitrates and Nitrites.

Sodium nitrate	very slightly soluble.
Posassium nitrate	very slightly soluble.
Ammonium nitrate	slightly soluble.
Barium nitrate	insoluble.
Bismuth nitrate	insoluble.
Lead nitrate	very slightly soluble.
Silver nitrate	soluble.
Potassium nitrate	very slightly soluble.

Carbonates.

Potassium carbonate	insoluble.
Sodium carbonate (anhydrous)	insoluble.

Sulphates and Sulphites.

Copper sulphate (anhydrous)	insoluble.
Potassium sulphate	insoluble.
Ferric sulphate (anhydrous)	insoluble.
Ferrous ammonium sulphate (crystalline)	insoluble.
Ferrous sulphate (anhydrous)	insoluble.
Calcium sulphite	insoluble.

Acetates.

Zinc acetate (crystalline)	soluble.
Copper acetate (crystalline)	slightly soluble.
Lead acetate (crystalline)	slightly soluble.
Magnesium acetate	insoluble.
Sodium acetate	insoluble.
Calcium acetate	insoluble.

Miscellaneous

Potassium ferricyanide	insoluble
Boric acid	freely soluble
Mercuric sulphide	insoluble
Potassium chlorate	very slightly soluble
Ferric pyrophosphate	insoluble
Ammonium molybdate	insoluble
Ammonium oxalate	insoluble
Ammonium tartrate	insoluble
Cupric chloride crystalline	freely soluble
Nickelous sulphate crystalline	very sparingly soluble
Lithium chloride crystalline	soluble
Cobaltous nitrate crystalline	freely soluble
Nickelous nitrate crystalline	sparingly soluble
Malic acid	freely soluble
Tartaric acid	freely soluble
Oxalic acid	freely soluble

The solubility at 25° C. has been determined quantitatively for the following

[illegible]	[illegible]
Potassium [illegible]	[illegible]
Potassium [illegible]	[illegible]
Mercuric [illegible]	[illegible]
Mercuric [illegible]	[illegible]
[illegible]	[illegible]

The [illegible] with [illegible] solutions [illegible] that with [illegible] solutions. The solubility [illegible] solutions [illegible] 25° C. [illegible] the same as that [illegible] [illegible] solutions.

[illegible]

[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, DEPARTMENT OF AGRICULTURE, No. XXII.]

[*Contributed by H. W. Wiley.*]

NOTE ON THE SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF ACETONE.*

BY K. P. MCELROY AND W. H. KRUG.

In the following table are given the specific gravities of acetone solutions as determined for every five per cent. Determinations were made in a piknometer carrying a thermometer stopper, and were all done from duplicate solutions. The acetone used had a boiling point of 56.4. It was prepared from the crude acetone sold by Hasslacher, in New York, by boiling the redistilled article over calcium chloride under a reflux for three days, and then distilling. Samples prepared by first converting the acetone into acetone-sulphite of soda, liberating the acetone with sodium carbonate, distilling, dehydrating, and again distilling, gave figures identical with the acetone used. Acetone purified by allowing a dilute solution to stand over permanganate for a day, dehydrating, distilling, etc., gave closely agreeing figures. In the tables, specific gravity is taken to mean the weight in grams of 1 cc. (not corrected for vacuo) at the temperature of observation. In other words water at 4 is taken as unity. The values given by Rosseti's table (*Biedermann's Chem. Kalendar*, **26**) for the density of water at different temperatures were used to determine the capacity of the piknometers.

Table.

Per cent. Acetone.	Weight of 1 cc. in Grams at 15°.	Weight of 1 cc. in Grams at 20°.	Weight of 1 cc. in Grams at 25°.
100	79726	79197	78630
95		80748	80205
90		82197	81653
85		83588	83073
80		84981	84454
75	86442	86129	85533
70	88085	87545	87073
65	89271	88785	88282
60	90447	89953	89477

*Read before the Washington Chemical Society, March 10, 1892.

solution, the rule which had been observed with other solutions, viz., that the solubility decreases with a rise in temperature, was reversed.

In a 10 per cent. dextrose solution, the solubility of acetone increases as the temperature rises, while in more concentrated solutions the solubility follows the common rule.

The solubility in 10, 20 and 30 per cent. sugar solutions was also determined, and this was found to act similarly to maltose.

It seems, therefore, that sugars of the group $C_{12}H_{22}O_{11}$ behave similarly with acetone, while sugars of the group $C_6H_{12}O_6$ act differently from the above.

Solubility of Acetone in Dextrose Solutions.

100 Gms. Dextrose Solution Dissolve Gms. Acetone at

Per Cent. Dextrose.	15°	25°	35°
10	736.75	747.86	761.54
20	255.28	247.71	240.80
30	157.54	149.83	142.53
40	86.95	79.57	74.03
50	36.16	33.02	31.18

Solubility of Acetone in Maltose Solutions.

100 Gms. Maltose Solution Dissolve Gms. Acetone at

Per Cent. Maltose.	15°	25°	35°
10	353.63	348.09	342.03
20	185.40	181.17	176.86
30	119.90	115.99	112.37
40	78.35	74.73	70.53
50	46.17	42.95	39.82

Solubility of Acetone in Sucrose Solutions.

100 Gms. Sucrose Solution Dissolve Gms. Acetone at

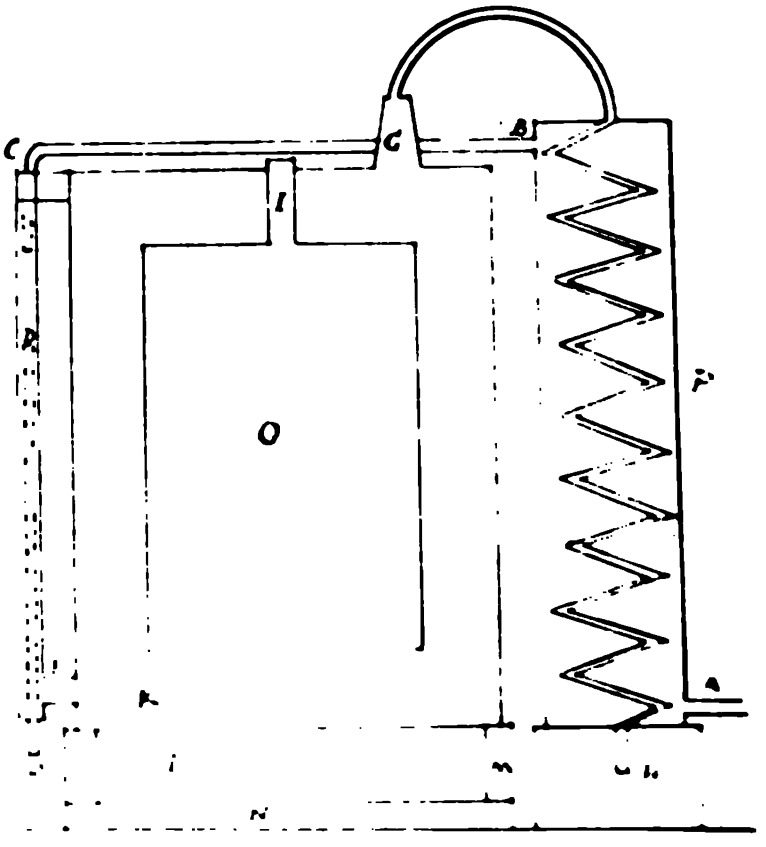
Per Cent. Sucrose.	15°	25°	35°
10	597.23	581.84	574.84
20	272.53	263.19	251.82
30	172.40	162.55	150.61

April 13, 1892.

A NEW WATER OVEN AND STILL.

By Herbert M. Hill

I have been using the water oven and still shown below for the past year with great satisfaction. I do not know that the idea is original, but the combination is certainly a success, being very economical and rapid in its action from the fact that the water for oven and still is delivered almost at boiling temperature for use



[illegible] the middle line parallel to [illegible] from the city supply [illegible] in the condenser passing [illegible] into the top of the glass

constant level tube *C*. *D* is the inner tube, the height of the tops of which determines the water level in the still. *E* is the metal tube making connection with the interior of the still. *F* represents the outlet for attachment of pipe to carry off waste water. *G* is a steam dome, serving for the attachment of the condenser tube, and to prevent water drops, projected from the boiling water, passing over with the steam. The condensed water runs from *H* and is preserved in a stoppered carboy placed beneath the table on which the condenser rests. *I* is tube for thermometer, and *K* water space.

The whole rests on a foundation of brick, and is heated by a Fletcher burner, using natural gas. The oven is of heavy copper, tin lined, with condenser of zinc with a coil of block tin.

From our ordinary use of the oven in drying operations, we have an abundant supply of distilled water besides, and when once set in operation, the further action of still and oven is automatic.

CHEMICAL LABORATORY,
UNIVERSITY OF BUFFALO.

[CONTRIBUTIONS FROM THE LABORATORY OF FRED. C. WELLS, SAVANNAH, GA.]

ON THE STANDARDIZATION OF ACID FOR THE KJELDAHL DETERMINATION OF NITROGEN.

In view of the importance of a correct standardization of the acid in the above method, it seems of interest to compare the methods recommended by the Association of Official Agricultural Chemists with each other and with others commonly adopted.

M. A. Scovell, in his opening address to the Association, reported results obtained by A. M. Peter, reduced to terms of nitrogen in a one-tenth normal solution of ammonia.

My determinations were made in a solution of hydrochloric acid containing approximately 10.43 gm. of HCl to the liter.

For convenience of comparison, I have reduced Peter's results to an acid 2.8 × one-tenth normal HCl.

The results so obtained were gravimetrically with $AgNO_3$, 10.26 gms. HCl to the liter.

Volumetrically with tetroxalate of potassium, 10.35 gm. to the liter.

By distilling NH_4Cl with an excess of NaOH, [illegible] liter

My results are given in the following table

No.	Substance determined	Method	[illegible]	[illegible]
1	HCl solution.	Gravimetrically		[illegible]
2	"	"		
3	"	Volumetrically with $AgNO_3$ 3 determinations	K_2CrO_4	[illegible]
4	"	Distilling NH_4Cl with NaOH	[illegible]	[illegible]
5.	"	"		[illegible]
6	"	$NaHCO_3$		[illegible]
7				[illegible]
8	NH OH solution	Oxalic acid bought as p	[illegible]	[illegible]
9	"	Oxalic acid carefully prepared 2 determinations		[illegible]
11		H_2SO_4	[illegible]	[illegible]
12				[illegible]

Determinations 11 and 12 were made with two samples [illegible] placed at my disposal by Mr. B. F. Lamoy [illegible] this [illegible] ized by himself against carefully prepared Na_2CO_3 [illegible] different times

Determinations with iodide and iodate of potassium [illegible] lower than the gravimetric method

I found [illegible] useless as an indicator for oxalic [illegible] ammonia

The difference between the gravimetric method and [illegible] with NaOH is according to Peter [illegible] my [illegible]

The [illegible] results and the close agreement [illegible] my results with [illegible] demonstrate that the [illegible] due to the method [illegible] results [illegible] volumetric determination [illegible]

[illegible]

plies to the tetroxalate, viz., that containing crystal water, it is liable to alter in keeping. Peter's results for the tetroxalate method were .04 gm. to liter lower than those obtained from distilling NH_4Cl with NaOH. The results which I obtained from Na_2CO_3, $NaHCO_3$, and from $H_2C_2O_4$ were from .01 to .03 gms. less than by distillation, or practically agreeing with Peter's.

It seems safe to conclude:

1st, That the gravimetric method gives too low results.

2d, That distillation of an ammonia salt with NaOH gives too high results.

3d. That the true value of standard solutions may be obtained very closely with either soda, tetroxalate of potassium, oxalic acid, or bicarbonate of sodium.

Tetroxalate of potassium possesses all the disadvantages that pertain to all the above-mentioned reagents. It is harder to purify than soda, and it "weathers" as readily as oxalic acid.

Bornträger's article came to hand too late for me to embody experiments on acid tartrate of potassium in this article.

ON CARMINE SUGAR.

Hlasiwetz and Grabowski found in cochineal a sugar to which they gave the name "carminzucker," and assigned the formula $C_6H_{10}O_5$ at 50°, $C_6H_8O_4$ at 100°. (Annalen, **141**, 338.)

In hopes of identifying the sugar with some of the better-known glucoses, I subjected cochineal to oxidation with concentrated nitric acid. Among the oxidation products, I discovered oxalic acid, but no mucic or saccharic acid; on purifying according to Hlasiwetz and Grabowski, I obtained a liquid reducing Fehling's solution and giving no reaction; with a solution of fuchsin decolorized with SO_2, on distillation with acids, I obtained a red coloration in the distillate with acetate of anilin.

*It must be noted here that Wehmer and Tollens obtained no levulinic acid from pure carmine acid. It seems to me evident that the so-called carminzucker is one of the pentoses, and as Hlasiwetz and Grabowski failed to observe any optical activity, probably xylose.

*Ber. **19**, 708.

PYRITES AS A MATERIAL FOR THE MANUFACTURE OF SULPHURIC ACID

BY J. H. KEITH

I am inclined to think that Mr. W. H. Adams [illegible] "Pyrites as a Material for the Manufacture of Sulphur" [illegible] in the February JOURNAL has given to pyrites an advantage [illegible] brimstone as a material for the manufacture of sulphuric [illegible] which I do not think it possesses except in many [illegible] copper may be obtained advantageously from the pyrites.

In the first place he places the cost of pyrites at [illegible] ton, a better average being from six to eight dollars [illegible] immediate mining district, while the price of brimstone [illegible] at twenty-four dollars per ton, which is perhaps [illegible] anything a little high, being more correct from twenty [illegible] twenty-four dollars per ton. The uncertainty of the supply [illegible] rites in this country is a further disadvantage in the use [illegible] material.

In the second place in the manufacture of sulphuric [illegible] brimstone he uses six per cent of nitrate of soda [illegible] twenty-four and a half per cent, while it is [illegible] that among [illegible] plants [illegible] [illegible] [illegible]

[illegible]

[illegible]

generally calculated to be at least one-third larger. Moreover, the life of the chamber is calculated to be from fifteen to twenty years with brimstone, but only from ten to fifteen years with pyrites as a material.

I had charge of sulphuric acid works for four years, using at first pyrites, afterwards brimstone, and it was after thorough study and examination of the works, both in Atlanta, Ga., and Charleston, S. C., that we changed from pyrites to brimstone, and were rewarded by being able to produce more and cheaper acid per day with the same chambers than before. We used pyrites from Georgia, Virginia, and the Northwest, the latter being superior, but the supply too uncertain.

BENTONVILLE, ARKANSAS.

APPLE JACK, OR APPLE BRANDY.

BY S. C. UPSON, JR.

The manufacture of apple jack or apple brandy is quite a large industry in some parts of Virginia, Northeastern Georgia, North Carolina, Tennessee, and New Jersey, and, in fact, in every locality where the cultivation of apples is carried on.

At convenient localities there are usually licensed distilleries, to which the farmer hauls his apples, and in return receives the apple brandy which they produce, less, of course, the toll of the distiller.

The following is a description of the method employed at a large apple brandy distillery in Virginia. The distillery itself is a regular whiskey distillery outfit, with the addition of a large cider press.

There are two methods of making the apple-jack, and hence the brandy itself is known by two names, *i. e.*, apple-jack and jug brandy, according to the method employed in its production.

The usual method is to mash the apples and express the cider in the cider press. This cider is then allowed to stand in barrels under a shed, in the open air, until it becomes "hard cider." This usually takes, in dry autumn weather, from ten to eighteen days, according to the temperature of the air at that season. The cider is then taken into the distillery and distilled.

The first distillate is called technically "singlings" or "low wines." This is then redistilled, which gives apple-jack.

The second method consists in simply mashing the apples, and

allowing the cider and mash to ferment together in large [illegible] heads, under sheds. This takes about thirteen to fourteen [illegible]

The mash and cider are then put in the boiler and distilled.

But to keep the mash, which settles firmly at the bottom [illegible] boiler, from burning and thereby giving to the brandy a [illegible] greeable, bitter, and smoky flavor, the distillers add wood-ashes, which, mixing with the gummy residue, keeps it from adhering to the bottom. The boiling of the liquid keeps the residue in constant agitation. When pine wood ashes are used they impart to the brandy a resinous flavor, and this liquor is known as "Pine-top Brandy." Sand can be substituted for ashes but it quickly wears out the copper boilers.

Sweet apples yield the most brandy.

The correct judging as to the time when the cider has arrived at the proper state of fermentation is of importance in making the largest amount of brandy. If it is allowed to stand too long or at too high a temperature, the cider spoils [illegible] on the acetic fermentation [illegible]

It takes about hundred bushels of apples [illegible] to produce about one gallon of apple-jack, which [illegible] less than one half the total production.

Apple brandy, which [illegible] at the [illegible] per [illegible]

[illegible]

[illegible] New Jersey [illegible]

[illegible]

15.

SULPHUR-MINING IN SICILY.*

REPORT BY CONSUL HEATH, CATANIA.

The mining and fusing of sulphur ore in Sicily has been carried on for a great many years, but from lack of enterprise and for want of outside capital, which cannot be induced to invest in any enterprise on the island, the mining and fusing is still carried on in the most primitive fashion. In the majority of mines machinery is unknown, and in the larger and more valuable ones only pumps and hoisting apparatus are used. Hand labor is universal, and a great many children find employment in carrying in baskets on the head the mineral from the mine to the surface.

There are practically four systems of melting sulphur in Sicily —the Calcherone, the Sinopoli furnace, the steam process, and Gill's furnace. The first two are most largely used, because it requires little or no capital to fuse in this way. They have a great many disadvantages, however, viz: The fumes kill or ruin all vegetation for miles in the vicinity; the sulphur rock being used for fuel in these processes, a large percentage of sulphur is consequently consumed, besides about 10 per cent. is still left in the mineral rock; then the product is not so valuable as in the other processes.

The steam process is a great improvement on the first two, but can only be used where the mineral is very rich and porous. No fumes escape to destroy vegetation, and the product is of a better quality. This process is comprised of large iron tubes filled with mineral, into which dry steam is injected.

Official experiments in two of the processes give the following results: Four cubic meters of mineral melted by the steam process have yielded 1,031 kilogrammes of sulphur; 4 cubic meters of mineral melted by the Calcherone process have yielded 932 kilogrammes of sulphur.

Gill's, an English process, has been tried extensively on the island, but I am now informed, is no longer used, because it required skilled assistance and only a small quantity of mineral can be treated at a time.

The Leon Gil y Ruiz patent Spanish process seems to be the most scientific and to give the best results. It has obtained the following perfection: Mineral for trial was chemically analyzed

*From Consular Reports, Nov., 1891.

and found to contain 15 per cent of sulphur; the product by Leon Gil's furnace was 12.22 per cent of sulphur and by the Calcheron process 5.6 per cent, thus leaving in the mineral only [illegible] per cent of sulphur, instead of 9.4 per cent by the Calcheron. The estimated cost per day of running a battery of thirty-two furnaces of the Leon Gil's patent is

Four firemen at 2 lire each	[illegible]
One engine-driver	[illegible]
Coal	[illegible]
Oil	[illegible]
Sundries	[illegible]
Cleaning steam boilers	[illegible]
Repairs machinery and ventilator	[illegible]
Total	[illegible]

In opening a mine in the United States to produce sulphur in competition with the Sicilian product two facts must be borne in mind. First, that the pay of labor is very low in Sicily; and second, that freight is equally low from Sicily to all seaports. Steamer freights for sulphur to New York, Philadelphia, and Boston are often lower than by sailing vessel, because the fruit steamers must have some heavy cargo or ballast. In a recent report I mentioned that the freight on a box of oranges from Catania to New York was only one-fourth of the freight on a similar box of oranges from Tampa, Fla., to New York. The steamers from Sicily make their profit on the orange and lemon freights, and are willing to carry more money on the sulphur freight for the reason that they must have ballast.

I appended a letter from the United States consular agent at Leghorn, [illegible] mining engineer, explaining the Sicilian process. Mr. [illegible] is the owner of sulphur mines and speaks from actual knowledge.

[illegible]

ings for regular work. Daily experience proves that it is foolish to rely too much on the richness and importance of a sulphur vein, that may change from one moment to the other, causing the total loss of the investment made. There are very few mines in Sicily deserving the expense of a regular and complete outfit, and in the best cases the greatest economy must be used, always bearing in mind that a sulphur mine worked with activity will not last long.

The cost of mining cannot be stated with exactness, because all the mines do not present the same difficulties. In fact, many of them are from 200 to 300 meters deep, while others can be worked at from 20 to 30 meters below the surface of the earth. The quantity of water to be pumped out, the hardness of the materials covering the brimstone ore, and the direction and dimension of the seams cause greater or less expenses. Nevertheless, I think I am not very far from the truth when I state that the mean cost for obtaining a ton of brimstone is as follows:

Mining and hoisting	33
Melting	8
General expenses	5
Total	46

To this should be added the Government and town dues, reaching as high as 30 per cent. of the profits.

The transportation to the seaports is made partly by carts and mules and partly by railway. The freight varies according to distance. The shipping expenses have not varied much during the last 3 years, and are as follows:

Cartage from the railway car and storage in warehouses, per ton,	0.80
Transportation on lighters . . . . . do . .	2.10
Customs dues	12.00
Chambers of commerce dues	.25

The commission of the shipping agent is 1 ½ per cent.

Crude brimstone, as exported by the United States, is divided into seven different qualities, or grades. The difference between two such grades amounts to little more than 30 cents per ton.

The market price of brimstone changes daily, and, therefore, it is not easy to state the exact price which has ruled during the last 3 years. But we may reckon that the prices during 1888–'89 remained nearly steady at about 71 lire per ton, free on board, duties and commission extra. During last year the price ranged from 66 lire in the first months to as high as 101 lire in the last months.

Sulphur in Sicily is only refined in Catania; therefore, you can obtain personally full information on the different methods in use.

The Sinopoli furnace, mentioned in your dispatch, seems to have given satisfactory results. Inclosed you will find a letter with a full and complete description of this furnace.

ARTHUR VERDERAME,
Consular Agent.

UNITED STATES CONSULAR AGENCY,
LICATA, July 15, 1891.

ENGINEER INGRIA TO CONSULAR AGENT VERDI RAMP

I answer with some delay your letter asking for a description of the Sinopoli furnace, as important business has prevented me from doing so earlier.

The Sinopoli furnace is composed of six or more cells with vertical walls made of iron plates, in which the mineral is placed. These cases are about 2 meters long, 1 meters high, and 0.25 meter wide, and are placed one over the other, separated by a space of 12 centimeters. They are walled up as an oven around which are two fireplaces at different levels. The heat entering from the upper part into the above mentioned space 12 centimeters and passing over the walls of the cells increases the temperature to the melting point.

After the cells are filled with broken mineral they are covered with a stratum of wet chalk, with a hole in each box. These holes are used as outlets for the vapor and gases contained in the mineral. [illegible] and after all vapors and gases are allowed to escape the intensity of the fire is diminished, continuing so for for 18 hours. When the [illegible] of the melted mineral commences to flow off from the front wall of the [illegible] through a hole punctured in its lower part.

About 36 hours are needed for the whole operation. The [illegible] contained in the six cells ordinarily does not exceed 18 tons. But by increasing the number of cells and consequently the width of the furnace the quantity of the mineral increases in proportion.

According to Engineer Matteucci's experiments the following results have been obtained: Average yield with the calcarone system [illegible] per cent; average yield with the Sinopoli system [illegible] per cent, an increase of [illegible] per cent which at the price of [illegible] lire per ton represents in the mere wood [illegible] besides the improved quality.

Engineer Matteucci [illegible] the necessity of [illegible] and commercial [illegible] adapted to the improvement [illegible] above [illegible]. Two furnaces should be built under the same roof 2 [illegible] between the walls [illegible] these two furnaces [illegible] the upper part [illegible] the lower part [illegible] the heating [illegible] the walls [illegible] with a capacity [illegible] meters each [illegible] the average yield [illegible]

Engineer Matteucci [illegible] the Sinopoli apparatus presents a [illegible] advantages [illegible] treat [illegible] the [illegible] process [illegible]

[illegible]

[illegible] STATION [illegible]

[illegible] with the calcarone [illegible] with [illegible] the Sinopoli apparatus [illegible]

The estimate of $9 per ton is for mining and bringing to the surface the mineral and fusing it on the spot ready for market.

Refining sulphur is another branch of the trade. The process and costs are kept secret.

Transportation.—The cost of transportation varies in each mine. The modes are by railroad, when the mine is in the vicinity, by mule back, and by private narrow-gauge railroads from some of the richest mines.

Exporting.—In Catania lighterage or cartage is about 10 lire per ton. The export duty is 10 lire per ton.

Prices.—Prices to-day for all grades of Licata sulphur, unmixed, in store at Catania, are as follows per 100 kilogrammes:

Description.	Price.	Description.	Price.
	Lire.		*Lire.*
First grade (best)	10.71	Third grade:	
Second grade:		Best	9.85
Best	10.57	Good	9.77
Good	10.44	Current	8.70
Current	10.12		

The highest and lowest prices for third-grade (best) sulphur, in store at Catania, during the varions months of the last 3 years was as follows:

Month.	Price.	Month.	Price.
1889.	*Lire.*	1890—Continued.	*Lire.*
January	8.61 to 8.45	May	9.01
February	8.91 to 9.01	June	8.99 to 8.97
March	8.87 to 8.85	July	8.96 to 8.91
April	8.90 to 8.83	August	8.95 to 8.91
May	8.84 to 8.24	September	8.49 to 8.48
June	9.35 to 9.02	October	8.51 to 8.43
July	8.75 to 8.71	November	8.57 to 8.44
August	8.90 to 8.85	December	8.90 to 8.67½
September	8.80 to 8.79	1891.	
October	8.60 to 8.53	January	9.48 to 9.37
November	9.00 to 8.98	February	9.51 to 9.50
December	8.97	March	9.41 to 9.40
1890.		April	9.23 to 9.21
January	8.90 to 8.86	May	9.27 to 9.11
February	8.87 to 8.86	June	9.04 to 9.03
March	9.05 to 9.04	July	9.37 to 9.23
April	9.23 to 9.21		

BUSINESS METHODS

The merchants in Sicily make a price, cost, and freight against London bankers' credits. They first get refusal for the quantity desired from the warehouse owners, and, as the freight is a known quantity in transactions by cable, the merchants generally claim the option of shipping at any time during [illegible] days.

EXPORTERS

Some of the principal exporters of Sicilian sulphur are: [illegible] ter, Catania; Alonzo & Consoli, Catania; P. [illegible], Catania; F. Baller & Co., Messina; E. Fog & Son, Messina; [illegible] Wedekind & Co., Palermo; Young Bros., Palermo. These parties will furnish market reports if stamp is inclosed for reply.

Sulphur is always shipped from Catania, Licata, and Girgenti. The principal shipping merchants are at Catania and Messina.

SUPPLEMENTARY REPORT

Mr. Edward A. Oates, of Porto Empedocle, the leading statistician on sulphur products, has kindly given me the following information:

> [illegible]
>
> [illegible]

[illegible]

The following is the report on methods for refining sulphur by the Italian Goverment mining engineer.

THE CALCHERONE

This process is the one mostly used. In the province nearly 65 per cent. of the sulphur is obtained through the Calcherone, because it offers the great advantage of little expense in building, and even the cost of fusing is greatly reduced, thus obtaining a good product in a very short time. It can be made of any size and capacity, from 40 to 50 cubic metres to 250 and even 300 cubic metres.

GILL'S FURNACE.

The use of Gill's furnace is extending rapidly, as it is found of great advantage in small, as well as in large, mines. About 25 per cent. of the sulphur produced in the province is obtained by this system. It further offers the advantage of permitting the fusion as soon as the mineral is extracted, because it produces very little smoke and generally is of no damage to anyone. It is, however, subject to the law of 1851, by which, in case of damage, its use must be discontinued. With a certain kind of mineral it gives an increased production, much to the detriment, however, of the quality. For setting up one of these furnaces a heavy outlay is required, especially if a permanent one is needed. Even the cost of fusing is higher than with the Calcherone. It can be constructed either with three or four cells, but the one with four cells is always preferred.

OTHER FURNACES.

Other furnaces under experiment are as follows :

Di Stefano's furnace.—This furnace has six cells. It is similar to Gill's furnace, as far as the passing of the gas is concerned, but the alimentation of the air is not constant, and the condensation of the gaseous product is brought to the highest degree. No practical results are known as yet, but certainly it will be preferred to Gill's furnace as its workings are less dangerous.

Duletta & Constanzo's furnace.—This furnace has four cells. The alimentary air in this system, does not pass through the burning coal, but is heated in passing through a canal around one of the cells in fusion. No results are known.

Various patented systems, as Perelli's', etc., are now discarded.

Steam furnace.—This furnace is used in different important mines, and nearly 10 per cent. of the sulphur is so obtained To build one of these furnaces a great expense is required, and skilled people are necessary to work it. It has, however, the advantage of immediately fusing the mineral extracted, but the yield is not larger than that obtained with the Calcherone, although the quality is superior by 2 degrees. The cost of fusing is also higher, but equal to that of Gill's furnace.

CHARLES HEATH,
Consul.

UNITED STATES CONSULATE,
CATANIA, September 2, 1891.

A RAPID METHOD FOR PHOSPHORUS DETERMINATION IN IRON, STEEL, AND ORES *

By James O. Handy, Chemist of the Pittsburg Testing Laboratory.

No method of determining phosphorus will find favor among chemists unless it possesses advantages over existing methods. While retaining the accuracy of the best methods now known, it must be simpler, more rapidly executed, or less expensive. My belief that the process which I have worked out is a step in this direction, is my reason for now describing it.

I owe to Mr. C. E. Manby's paper, in the J. A. & A. C. for February, 1892, the suggestion of essential points in my process. The method which he gives is too long, and would not compare with the Emmerton-Brown-Jones method (A. I. M. E., February, 1892), which can be executed, with proper appliances, in thirty minutes, or less. Mr. E. F. Wood's latest method, a gravimetric one, is said to yield results in twenty minutes. I do not know how uniformly reliable these results are. I believe that they are always checked by a longer method.

I have proved by a great many experiments, that several of the steps of Mr. Manby's process can either be safely dropped, or simplyfied, and a rapid and satisfactory process produced.

My method consists of the following points:

1. Separation of the phosphorus as pure phosphomolybdate of ammonium, by washing with neutral potassium nitrate solution, after the regular washing with 1 per cent. nitric acid.

2. Solution of the pure phosphomolybdate in a measured volume of standard sodium hydrate solution. A definite portion of the alkali is taken up in neutralizing the phosphomolybdate.

3. The excess of the alkali is measured by means of standard nitric acid. Phenolphthalein is used as the indicator. The end reaction is very distinct. Duplicate analyses give closely concordant results, which agree exactly with determinations of phosphorus made by other methods. With no any special appliances, and with [illegible] easily be done in thirty minutes. [illegible] can be shortened to half [illegible] Mr. [illegible]

[illegible]

The first part of the process is essentially that of Dr. Drown (A. I. M. E., June, 1889). I have confirmed, by long experience, Dr. Drown's statement that sugar can be safely used as a reducing agent in the process. Clemens Jones substituted ferrous sulphate, but I find that it requires several times as much ferrous sulphate as sugar for reduction, and that the sugar produces no ill effects. Pure granulated sugar is used.

THE METHOD.

Dissolve 2 gms. of steel in a 12-ounce Erlenmeyer flask, in 75 cc. of nitric acid (1.13). To the boiling solution, add 15 cc. of permanganate solution (5 gms. per liter). Boil until pink color disappears. Oxidation of the carbon and phosphorus is complete if there remains a brown precipitate of oxide of manganese. More permanganate will be required only in the analysis of iron or steel of very high carbon. Remove flask for a moment from the light. Add about $\frac{1}{30}$ gm. of granulated sugar. Replace flask on the light and heat till the solution clears. Take flask off the light, and, after two or three minutes, add 13 cc. of .90 ammonia. If the latter is poured carefully down the side of the flask, no loss by spattering will occur. Agitate the flask-contents till, in a moment, the ferric hydrate is redissolved. Insert thermometer, and cool (or warm) to 85 degrees centigrade. Add 50 cc. of molybdate solution, causing it to rinse off the thermometer as it flows into the flask. Insert rubber stopper. Wrap flask in towel, or put it into a shaking-box, and shake it for five minutes. Filter immediately, using a 9 cm. Swedish filter, and moderate suction. The precipitation is complete, and the precipitate shows no tendency to run through the filter. Wash out flask, and wash the filter and contents five times with 1 per cent. nitric acid; wash five times with $\frac{1}{10}$ per cent. potassium nitrate wash (1 gm. per liter). Place filter and contents in the flask. Add from a pipette 10 or 20 cc. of standard sodium hydrate solution. Shake for a moment, until the yellow precipitate is dissolved. Dilute with water to about 50 cc. Add 3 drops phenol-phtalein solution and titrate with standard nitric acid till the pink color disappears. The cubic centimeters of standard sodium hydrate used up in neutralizing the yellow precipitate represent the hundreths per cent. of phosphorus in the sample analyzed.

REAGENTS

Molybdate Solution – E. F. Wood's 1888 formula – [illegible] g. of molybdic acid is mixed with 1200 cc. of water in a stoneware [illegible] 700 cc. of ammonia (.90 sp. gr.) are stirred in and the stirring continued till all soluble matter is dissolved. [illegible] cc. of nitric acid (sp. gr. 1.42) are added to partially neutralize the ammonia in the solution. In each of four 2½ liter bottles is placed a mixture of 500 cc. nitric acid (sp. gr. 1.42) and 1200 cc. of water.

Pour 550 cc. of the molybdate solution through a funnel into each bottle, and mix the contents by a slight rotating motion. If the stream of molybdate flows quickly and continuously into the acid mixture, no separation of molybdic acid takes place. Both solutions may be hot when mixed.

I have used this formula for three years with uniform success and have seen it in continuous use in many other laboratories. Little or no separation of molybdic acid takes place in stirring, but we always filter it just before using.

FILTER PAPER

No. 1 (F.) Munktell's Swedish filter paper has given us entire satisfaction. We are much pleased with its uniformity.

Nine cm. filters are used.

PURE YELLOW PRECIPITATE

This can be prepared from acidified ammonium molybdate solution by precipitating with molybdate solution. Wash the precipitate with 1 per cent nitric wash. Dry at [illegible] C. [illegible] Keep in glass stoppered bottles for use.

Use one tenth gm. for standardizing the sodium molybdate solution by working on stocks containing from [illegible] per cent of phosphorus. For high phosphorus work use a quarter to [illegible] phosphorus, which is approximately equal to the amount [illegible] from the [illegible] of the metal. This prevents [illegible] which is added [illegible] This excess would be [illegible] would have no significant [illegible] keeping this precipitate in the [illegible] passed through a wide range [illegible]

When the method is once established in a laboratory, the standardization of the sodium hydrate solution may be more conveniently done by means of steel or pig-iron of known phosphorus contents.

STANDARD SODIUM HYDRATE.

15.4 gms. of sodium hydrate are dissolved in 100 cc. of water. Saturated barium hydrate solution is stirred into the sodium hydrate solution until no more precipitation occurs. Filter at once and make up to two liters with distilled water. In practice, I shall make up 154 gms. of sodium hydrate at once, freeing it from carbonate as above and make up 2 liters. 200 cc. of this, made up to 2 liters will make the standard approximately.

STANDARD NITRIC ACID.

For a *stock solution*, make up 200 cc. of nitric acid (sp. gr. 1.42) to 2 liters. 200 cc. of the stock solution is made up to 2 liters for approximate standard. Run the standard alkali and acid against each other, and having ascertained their relative strengths, add sufficient water to the stronger of the two to make the solution equal in value.

Next run the sodium hydrate solution against .1000 gm. pure ammonium phospho-molybdate = .00163 gm. phosphorus. If its strength is too great (*e. g.*, if 1 cc. = .00206 gm phosphorus) add to 2 liters of the standard sodium hydrate 60 cc. of water. In order to preserve the equality of the acid and alkali solutions, add to 2 liters of the standard nitric acid 60 cc. of water and mix. The solutions will then be equal and 1 cc. = .0002 gm. of phosphorus or $\frac{1}{100}$ per cent. phosphorus, when 2 gms. of the sample are taken for analysis.

PHENOL-PHTALEIN INDICATOR.

Five-tenths gm. of phenol-phtalein are dissolved in 200 cc. of 95 per cent. alcohol. Use about 3 drops for each titration.

We feel sure that the phospho-molybdate of ammonium, as we obtain it in this process contains, when dried at 100° Centigrade, 1.63 per cent. of phosphorus. Our reasons are as follows:

1. Mr. E. F. Wood finds 1.63 per cent. phosphorus in the phospho-molybdate obtained by his method and dried at 100° Centigrade. (See J. A. C., 1888).

2. We have found by hundreds of analyses the absolute agreement of results by Mr Wood's process with those by Dr [illegible]'s (A. I. M. E., 1880) process, modified by *weighing* instead of *[illegible]ting* the yellow precipitate

3. Dr Franz Hundeshagen, in a very elaborate series of [illegible] (Z. A. C., 1880), finds that phospho molybdate precipitated and purified, as we do it, has 1·63 per cent of phosphorus when *dried at* 150° *Centigrade*

4. We find that pure phospho molybdate *dried at* [illegible] *grade* suffers no further loss of weight when *dried at* [illegible] *grade*. Hence we have two authorities to prove that the phospho-molybdate as we obtain it contains 1·63 per cent phosphorus

5. We find the results obtained by precipitation at temperatures from 20° to 85° Centigrade are identical

6. We find that samples precipitated at 85° Centigrade can be filtered immediately and correct results obtained, while at lower temperatures longer standing is needed before precipitation of the phosphorus is complete

7. We find by experiments on a sample of steel containing [illegible] per cent of arsenic that the phosphorus can be correctly estimated by our method without added precaution

8. We find perfect agreement between results by weighing the yellow precipitate and results by titrating the same by our method

Tables of results of some of the experiments by which we established the accuracy of the method are given below

	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

The last sample contains, according to Messrs. Booth, Garrett, & Blair, phosphorus .097 per cent., arsenic .014 per cent.

DISCUSSION.

Mr. MANBY: I am very glad, indeed, to see that my method has been so quickly taken up and improved by Mr. Handy, and that he has obtained such good results with it. I hope that the investigations of your committee will confirm his results. I have made estimations with the method in forty minutes, but I am pleased to see that this time has been cut down one-half by Mr. Handy. I found that the presence of ammonium salts was prejudicial to the accuracy of the titration, and I therefore resorted to the process of purifying the yellow precipitate by igniting it moderately over a lamp to expel ammonium nitrate. I consider the freeing of the yellow precipitate from acid and ammonium salts, by washing with $\frac{1}{10}$ per cent. potassium nitrate, a material improvement. I had feared to attempt titrating, with filter-paper suspended in the solution, but Mr. Handy's good results show that this fear was ungrounded.

The reaction which takes place when the sodium hydrate solution is added to the yellow precipitate, is an interesting study. I think that the yellow precipitate has the composition $(NH_4)_3PO_4$, 12 MoO_3. I believe *that the ammonia* in this compound *is replaced* by soda when excess of sodium hydrate is added. I think that with the conditions of dilution which we operate under, the ammonia would be held in solution.

Mr. VAN GUNDY: I believe that the soda *does not replace* the ammonia; for, if it did, then an exactly equivalent amount of ammonia would be set free, and the alkalimetric value of the resultant solution would be indentical with that of the measured amount of soda solution which was added. As practice shows that this is not the case, but, as the amount of soda used up varies with the amount of yellow precipitate present, I believe that the base of the soda unites directly with the phospho-molybdate of ammonia to form a neutral compound.

Mr. HANDY: I favor Mr. Van Gundy's theory.

Mr. MANBY: I believe that there is a certain amount of nitric acid which, ordinarily separates out with the yellow precipitate,

and *is not* removed by drying at 100° Centigrade, but is expelled by higher heat.

MR. HANDY: My experience and study do not let me [illegible] the presence of nitric acid in the yellow precipitate either [illegible] washed with 1 per cent nitric acid and dried at [illegible] or [illegible], when washed with 1 per cent nitric acid and then with [illegible] per cent potassium nitrate, and not dried. I prepared some yellow precipitate by washing with 1 per cent nitric acid and drying at 100° C. This material was placed in glass stoppered bottles to prevent reabsorption of moisture. Portions of this yellow precipitate exposed for a half hour to temperatures from [illegible] to 105° Centigrade in an air oven no loss of weight was [illegible] in either case.

In regard to the presence of nitric acid in the yellow precipitate after washing with 1 per cent nitric acid and then with [illegible] per cent potassium nitrate, I do not believe in it for the reason that almost identical results are obtained by titrating by my process the undried and dried precipitates. Slight variations were [illegible] sometimes obtained, but I found a higher value for the dried than the undried precipitates. These two facts I think effectually prove the presence of nitric acid in the yellow precipitate.

We have further the statement of Dr. F. Hundeshagen, [illegible] most elaborate research, Z. A. C. [illegible], that the yellow precipitate obtained by precipitation under conditions which are the same as we have in our method has the composition $NH_4 PO_3 12 MoO_3$, when dried at [illegible]. Nitric acid is in the [illegible].

MR. [illegible] MR. [illegible]: [illegible]

MR. [illegible] MR. HANDY: [illegible]

MR. [illegible]: [illegible] weight [illegible] yellow precipitate.

MR. [illegible]: [illegible] weight [illegible]

the yellow precipitate, dried on a filter at 100° Centigrade, is exposed to 150° Centigrade.

MR. HANDY: I believe that Mr. Carnahan's and Mr. Johnson's losses of weight were due to the oxidation of the carbon of the filter at the expense of the oxygen of the molybdate. This action is evidenced by the progressive blueing of the filter and precipitate when exposed longer than three-quarters of an hour to a temperature of 100° Centigrade or over.

My experiments were made by heating pure yellow precipitate in porcelain crucibles. I thus avoided any error caused by filter-paper oxidation.

NOTES ON IRON IN BONE-BLACK.*

BY DR. BRUNO TERNE.

The freshly-prepared bone-black of the market yields on an average from 0.1 to 0.3 per cent. of iron in the form of metallic iron, originating principally from iron mixed with the bones gathered up by the junk dealers, another portion coming from the wear and tear of the bone crushers and mills, and a very little from the iron vessels used in burning the bones.

Having been in charge for the last fifteen years of one of the largest plants for manufacturing bone-black, I had never experienced any trouble with our product, on account of the iron, until several months ago, when one of our patrons complained of an excess of iron in our black, which, according to his investigation, had run up in one instance to one-half of one per cent.

This complaint was coupled with the assertion that an increase of 0.25 per cent. of iron above the average would materially impair the process of refining sugar.

This charge coming from a source commanding serious consideration, caused us to look into this matter thoroughly, but an examination of the literature of sugar refining, covering a period commencing with 1872 (*Wagner's Jahresberichte*) up to date, failed to disclose a single case in corroboration of the above-cited assertion.

The more I thought over the matter the more I became convinced that the complaint made against our black, that it impaired

*Proceedings of the Chemical Section of the Franklin Institute, J. F. I., April, 1892.

the work of refining sugar liquors, was merely a convenient pretext to shield some irregularities in the process of refining which otherwise would have to be shouldered at home. We all know that organic acids will dissolve iron, but in refining sugars the liquors should be free from acids or at least nearly made free by previous neutralization; the traces of free organic acids must certainly all be absorbed by the six or seven per cent. of carbonate of lime contained in fresh bone black. The fact that in the spent black the yield of carbonate of lime is reduced to three [illegible] per cent., and the yield of iron considerably raised, demonstrates clearly that fresh black operates to free sugar liquors from iron as well as other impurities.

In order to ascertain what effect a solution acidulated with organic acid would have on the iron in bone black, I prepared two solutions of citric acid containing respectively [illegible] per cent. and [illegible] per cent. of free acid.

The acidity of these solutions is so great that no sugar liquor entering filters will ever approach it in acidity.

I selected a black which had given by analysis a yield of [illegible] per cent. of iron, and made the following experiments:

[illegible] grams of black with [illegible] of citric acid solution [illegible]

[illegible]

[illegible]

I exposed the four flasks on the top of a steam heater [illegible] four hours to a temperature of [illegible] F., after which I treated the still acid solution of iron with potassium [illegible] and potassium ferrocyanide, but no trace of iron could be found in the solution.

Not satisfied with this, I kept the flasks for eighteen hours on a steam [illegible] temperature [illegible] F. The results of the two experiments were also [illegible] the same.

[illegible] sample of black large enough to plant a crop [illegible] I took [illegible] of the same [illegible] and the same [illegible] per cent. free [illegible] F. [illegible] impurities [illegible] solution showed [illegible] a

trace of iron with the most sensitive reagents (potassium sulphocyanide and potassium ferridcyanide).

I went still a step further and prepared a solution of iron in citric acid, 200 cc. of which contained 1.01 gms. of iron. I took 100 cc. and diluted to 500 cc.; I mixed the dark-yellow solution in a flask with 500 gms. of fresh regular sugar-house black, boiled up for thirty minutes, filtered and obtained a perfectly limpid solution which contained not a trace of iron.

This experiment proved to my own satisfaction that an accidental excess of 0.25 per cent. of iron in fresh black could not be charged with creating irregularities in the process of refining sugar liquors. But not being an expert in sugar refining I submitted this problem with the above results of my own researches to my friend, Dr. Arno Behr, now Secretary and Treasurer of the Chicago Sugar Refining Company, an acknowledged expert in this branch of chemical industry at home and abroad. I submit herewith an abstract of his letter:

CHICAGO, January 4, 1892.

MY DEAR DR. TERNE: * * * "Iron is a very objectionable substance to have in filtered sugar solutions, because the refined soft sugars which are produced from such solutions take on a more or less gray appearance, which reduces their value considerably compared with others, which are free from iron and of a bright yellow color.

"Colonial raw sugars contain sometimes a considerable amount of iron, and in the absence of good chemical methods for the removal of this iron from the unfiltered liquor, the refiner relies on the bone-black to absorb it.

"In some refineries the sugar solutions enter the black practically neutral, in others they are left a little acid, but this is of no consequence, for you have found yourself that new black will absorb the iron even from a strongly acid solution. Even old working bone-black contains enough carbonate of lime (three or four per cent.) to neutralize any considerable excess of acid. There is, however, a considerable difference in the behavior of new and old black. Say you want to filter 100 pounds of dry sugar over 100 pounds of bone-black. Say this sugar contains two to three hundredths of one per cent. of Fe_2O_3. The solution will come from

the new black absolutely free from iron, while from the old black half of it perhaps will be free, and the other half will contain it in increasing quantities.

"This will happen with properly neutralized liquor and without any fermentation having occurred. Even if the sugar solution enters the black free from iron, towards the end it will come on the old black containing iron.

"It works this way without any attempt having been made to wash the liquor out of the black. As soon as that is done matters become worse. Even from very good black the diluted sugar solution carries away a certain amount of iron.

"Now in working it is found that the amount of iron increases in the black with its age, and that in the same proportion the amount of iron increases in the liquor. There is no way of removing the iron once absorbed by the black.

There are three sources of iron in the black:

1. The iron originally contained in the black.
2. The iron in the raw sugar.
3. The iron taken up by the liquor and the black in the sugar refinery.

[illegible]

that an accidental excess of a fraction of a per cent. over the acknowledged unavoidable proportion of iron in new black, could be held accountable for any disturbance in the process of sugar refining, and to have my protest recorded with the section against such a claim.

This point has been fairly covered by my own experiments, and is clearly corroborated by the opinion of one of the most competent sugar chemists of this country.

Regarding the chemical methods of iron determination which are far too laborious to perform every day, I have been trying to find a method which could be carried on with sufficient accuracy without requiring previous chemical training.

I found that a boy with the help of a magnet, could, by exercising the necessary care, make a determination, sufficiently accurate for the daily control of a bone-black mill.

Take 100 gms. of the black and spread in a thin layer over a sheet of white paper, then plough through it with a good magnet (I am using a six-inch horseshoe) and it will be found that most of the iron will be picked up at the first few passes.

After repeating the passes of the magnet in every direction, carefully observing that no part of the mass is missed, in a very few minutes all the iron will have been gathered on the watch glass ready for weighing. The results thus obtained come sufficiently close to those obtained by chemical test to serve as a control upon the process of manufacture, as the following examples will show:

The following tests have all been made within the last four months:

		By Chemical Analysis. Per Cent. Iron.	By Magnetic Test Per Cent. Iron.
October,	1891	0.360	0.410
	1891	0.160	0.219
December,	1891	0.387	0.501
January,	1892	0.100	0.130
	1892	0.169	0.213
	1892	0.080	0.107
	1892	0.199	0.224

While the magnetic test is invariably too high, it is sufficiently close to control the work of the black mills. The adherence of particles of carbon to the iron fully explains the result.

Regarding the chemical determination of iron, I consider a previous incineration of the black necessary, because there is a possibility that traces of organic matter left in the fresh black may be mistaken for iron by the reduction of the potassium permanganate.

ON THE APPROXIMATE ESTIMATION OF UREA IN URINE.*

BY [illegible]

In January, 1884, the writer published a paper under the [illegible] caption (see Ephemeris, page 438). In this paper, after [illegible] viewing the character and importance of the subject, its difficulties, and what had already been done, a simple apparatus and method were offered whereby the process was brought within reach of the physician and well trained nurse, to be applied in the physician's office or in the sick room. The advantages claimed for this method were first, its simplicity of construction from materials within easy reach of all; second, that instead of attempting to measure the evolved nitrogen gas, a proceeding requiring special apparatus, and almost beyond the reach of the ordinary physician, the volume of water displaced by the gas was measured; and that instead of handling substances so inconvenient, [illegible] and dangerous to inexpert persons as bromine and [illegible], a reagent for decomposing the urea was substituted that was much more simple and convenient, free from trouble and danger, and to be found ready prepared almost anywhere. This reagent was the common Solution of Chlorinated Soda of the U. S. Pharmacopœia from the revision of 1880 to that of 1890 inclusive.

From the need for such a device for common clinical use, the apparatus soon went into professional use, not only in [illegible] in other countries, where the importance of its use was [illegible], and during the past eight years [illegible] reports of its use have not been wanting in [illegible].

But [illegible] long [illegible] after an absence of two years [illegible] Quantitative Tests [illegible] published in The New York Medical Journal for November [illegible] page [illegible] [illegible] that [illegible] and very [illegible] [illegible] Soda as a reagent [illegible]

Upon referring to his notes and his published paper, this writer felt very sure of his facts and results upon which the statements of his paper were based, for they had been abundantly verified by subsequent experience, but he had full confidence in this part of Dr. Bierwirth's work, and knew not how to account for the discrepancy, especially as Dr. Bierwirth had used Solution of Chlorinated Soda that was known to be fully up to the U. S. P. standard. Investigation was at once begun and the cause of the difficulty was soon found at a point least suspected. In the revision of the U. S. Pharmacopœia for 1880, published in 1882, the proportions of the ingredients directed for making the Solution of Chlorinated Soda had been changed, and no notice of the change had been given because the strength in available Chlorine was not changed, and available Chlorine was supposed to be the only standard of value in the preparation.

The Solution was admitted to the U. S. P. in 1840, and from that time until 1880 the proportions were 24 parts of Carbonate of Sodium to 12 parts of Chlorinated Lime, but in 1880 they were changed to 25 parts of Carbonate of Sodium to 20 parts of Chlorinated Lime,—a reduction of 60 parts of the sodium salt in 160. In former revisions the sodium salt had been in large excess of what theory required, and this excess was judged to be useless and was left out, while the available chlorine remained as before. As the Committee of Revision knew of no other use for the Solution than that of a disinfectant, and knew of no disinfectant effects from the excess of Carbonate of Sodium, they knew of no change by leaving out this excess, and therefore gave no notice of change. In this change they followed the German Pharmacopœia, adopting its proportions. In the judgment of the writer this change was a mistake. The preparation is a loose combination of its elements, and undergoes internal molecular change by keeping, but the analogy of many other better known instances in which an excess of one element prevents or retards change, leads to the probability that the excess here is important. And, it is not improbable that the excess plays an important part in the disinfectant action.

It is however now very certain that while the Solution of 1870 and revisions previous to that, having the excess, will decompose urea completely, the Solution of 1880, not having the excess,

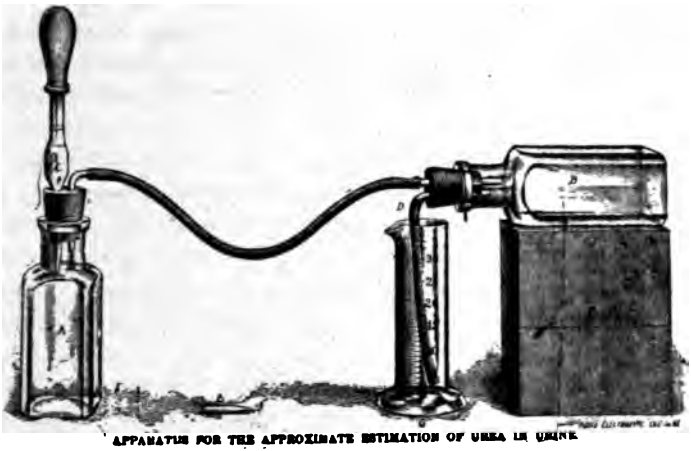
decomposes urea only partially, and this where both Solutions have the same proportion of available chlorine and the one answers perfectly for the writer's urea apparatus, while the other does not. And this difference in the Solution, is the sole reason of the difference in the results obtained by Dr. Bierwirth and the writer and the failure of the method is due, not to the apparatus [illegible] the reagent used in it. The original work of the writer was done late in 1883, and although the U. S. P. of 1880 was published in 1882, the change in making this Solution was not made until 1884 and was then made not through any appreciation on the part of the character of the change, but simply in obedience to the general practice of following the Pharmacopœia as a standard. How blindly this was done is still farther shown by the fact that the very formula and process of 1880 was reviewed by the writer in 1885 (see Ephemeris, page [illegible]) without noticing the change that had been made, the review having been directed to the Solution only as a disinfectant.

The change then being unknown and unsuspected and its relation to the decomposition of urea being of course [illegible] suspected, the writer made in his original paper the [illegible] and inaccurate statement that solutions made by either the Pharmacopœia of 1880 or of 1884 would answer very well for the purpose of which had the solution of the latter been used [illegible] trouble as has now been done by Dr. Bierwirth, it would [illegible] of course. How far the [illegible] have used the method [illegible] been misled by putting the wrong reagent [illegible] but it is [illegible] that the [illegible] statement was on the safe side.

The writer [illegible] Dr. Bierwirth [illegible] the solution [illegible] and [illegible]

[illegible]

First of all, it cannot be too strongly insisted upon that these rapid methods which are based on the decomposition of the urea and the measurement of its evolved nitrogen as the indication of its quantity, afford approximate results only. There are several errors incident to such processes in ordinary hands which are prac-



APPARATUS FOR THE APPROXIMATE ESTIMATION OF UREA IN URINE.

tically inevitable, and their due consideration shows conclusively that the general range of error can hardly be less than 0.1 per cent. above or below the truth, and should not be greater than about 0.2 per cent., plus or minus. That is, when a solution of pure urea of known strength is tested, the range of admissible error will not generally be less than 0.2 per cent., nor greater than 0.4 per cent. when 1 cubic centimeter is taken for assay, and about half that range when 2 cubic centimeters are taken,

APPARATUS.

The improved apparatus now offered is in principle and general design, the same as the old, but the quantity taken for the estimation is 2 cc. instead of 4, and therefore the vials are reduced to half the size formerly used. This is done, without materially increasing the error, by having a much smaller and more accurate capacity pipette, and by making this take the place of the urine jar by passing through the stopper, as shown in the cut. Then a graduated jar receives the water displaced by the gas, and measures it

directly with more accuracy and convenience than the graduated pipette.

The pasteboard box which contains the apparatus shown in the cut also contains a bottle of good chlorinated lime sufficient in quantity for forty testings. This bottle is dated on the bottom so that the age of the contents may be known. The lid of the box serves as a support for the bottle *B*. The box also contains a card with directions for the use of the apparatus. Another card with directions for making the different reagents, and a third card with urea table for interpreting results.

A large measure for taking the measure of daily urine, and two ordinary half pint bottles for mixing the reagent, are needed but not included with the apparatus.

In using the apparatus, put the reagent for decomposing the urea into bottle *A*. Then measure exactly 200 c.c. of the urine in the pipette. To do this properly, first dip the mouth of the rubber bulb into water, to lubricate it, and then slip it over the upper end of the pipette nearly as far it will go. Compress the bulb upon the pipette and dip the lower end of the pipette into the urine. Then relaxing the compression entirely, the bulb will expand and the urine will rise in the pipette to fill or nearly fill the body of it. Then holding the body firmly between the first finger and thumb, take the rubber ring at the mouth of the bulb with the right thumb and finger, and screw the bulb upward on the pipette until the urine rises to the mark, the lower limb of the meniscus to be exactly upon the mark, the lower point of the pipette being still kept immersed in the urine. Then raise the point of the pipette out of the urine, and screw the bulb a little higher on the pipette, so that the urine is drawn out of the point below. This avoids the risk of urine in the point, and an expansion of the air in the bulb [illegible] the urine out of the point. It is essential that the point [illegible] attempt the abstinent [illegible] the mark [illegible] compression of the rubber [illegible] the bulb [illegible] the rubber ring at the [illegible] the pipette [illegible] the last practicable moment [illegible]

ment, and that this error is multiplied from 500 to 600 times in applying the results of the assay to the total urine of twenty-four hours. And in processes where only 1 cc. of urine is taken for assay, the same error is multiplied from 1000 to 1200 times. The pipette, when thus carefully charged, is pushed through the vacant hole in the rubber stopper for bottle *A*, which stopper has just been dipped in water. This pushing through the wet stopper wipes off the urine from the outside of the pipette. The stopper thus prepared is then put into its place in bottle *A*. One end of the long piece of rubber tubing *C* is then dipped in water and slipped over the bent glass tube of bottle *A*, and from this it need not again be removed in subsequent testings. Next fill bottle *B* full of water of the temperature of the room, and then having slipped one end of the short piece of rubber tubing *D* over the bent glass tube of the rubber stopper of *B*, push the stopper into its place in the bottle, allowing the displaced water to escape through the tubes. Then holding bottle *B* in the right hand with the forefinger over the end of the straight glass tube, incline the bottle toward the bent glass tube until that and the rubber tube upon it fill with water. When filled, stop the flow of water from the rubber tube *D* by closing the straight glass tube with the forefinger, and with the left hand put the little glass stopper *E* into the free end of the rubber tube *D* while this tube is full of water. Then lay bottle *B*, thus charged, on its side, upon a support *F*, as shown in the cut, and slip the free end of the long rubber tube *C*, from bottle *A*, over the end of the straight glass tube of the stopper of bottle *B*, thus connecting *A* and *B*. Next remove the little stopper *E* from the end of the short rubber tube *D*, when a few drops of water will escape, and a few bubbles of air will enter *B* from *A*. But, if the apparatus be tight and be at the room temperature, no more water will run out nor will any air enter. Next, the measuring jar *G* is put under the short rubber tube, and this tube is lengthened or shortened by slipping it down or up upon the glass tube, until the end just clears the bottom of the graduated measuring jar; and now the apparatus is ready for the process.

THE PROCESS.

Taking bottle *A* in the right hand compress the rubber bulb

between the left thumb and fingers until the entire contents of the pipette are forced into bottle *A* with the reagent, and see that the last drop be forced in. Then still holding the bulb compressed shake the lower part of the bottle *A* from side to side, not up and down, for, beyond an accidental drop or two, nothing should get into the long rubber tube *C* to be carried over in the current of gas into bottle *B*. The reaction begins promptly, and while the gas is actively passing over into bottle *B* the compression of the rubber bulb of the pipette is to be gradually relaxed and the thumb and finger which compressed it are lowered to hold the lip of the bottle *A*. This part of the bottle is now kept quite steady, while the lower part is pretty actively shaken from side to side, and this shaking is to be continued as long as any bubbles of gas come over into bottle *B*. But if the shaking has to be continued longer than about ten minutes, the warmth of the hand will so warm the bottle *A* as to expand the air inside and cause a slow passing over of small bubbles. In cases of slow reaction, or end reaction, where ten or twenty minutes of shaking is required to make sure of the result, it is much better to have recourse to a warm bath for the bottle *A*. A bowl of hand warm water (about 40° C. or 104° F. or thereabouts) is to be used, and the bottle *A* being immersed in this is occasionally taken out and shaken until warmed up to the point where no more gas passes over. This will shorten to six or eight minutes a process which would otherwise go on for slow and tedious for half an hour. Whether the warm bath be used or not, the next step in the process after bubbles have practically ceased to come over is to remove bottle *A* from bath of water at the room temperature for [illegible] minutes. A vessel of water sitting upon a table in a room [illegible] will [illegible] must be used to maintain a temperature [illegible] C. below the room temperature, and such a [illegible] must be provided for this step. When bottle *A* has remained in water from *B* will [illegible] *A* is replaced in the water [illegible] and water [illegible] so that [illegible] the measuring [illegible] This [illegible] about 4 minutes in

mersion. The bottles and tubes are now lifted out and set aside, and the quantity of water in the measuring jar is carefully read off to one-half cubic centimeter.

EXPLANATION OF TABLE OF APPROXIMATE RESULTS.

Each cc. of the water in the measuring jar represents a cc. of the nitrogen gas evolved by the decomposition of the urea in the urine, and each cc. of the gas represents 0.0027 gm. of urea when the cc. of gas is measured at 0° C. and 760 mm. barometric pressure. The pressure may be disregarded in this process, but the expansion by temperature may not, although it was disregarded in the former paper and table. By the law of Dalton and Gay-Lussac gases expand $\frac{1}{273}$ of their volume at 0° C. for every 1° C., and as the measurement for this process may be assumed to be at about 18° C.=64.4° F., that temperature is adopted here. Thus $\frac{1}{273}$ of its volume for each degree multiplied by 18° C. is equal to 0.065934, and therefore 1 cc. of the gas measured at 0° C. measures at 18° C. 1.065934 cc., and this it is that is equal to 0.0027 gm. (.002688 gm. more exactly) of urea. Therefore from each cc. of water as read off from the measuring jar, 0.065934 cc. must be subtracted as a correction for temperature expansion. That is, the reading off is too high by this fraction from each cc., and for example 15 cc. as read off must be corrected by (0.0659×15=) 0.9885 cc., or practically 0.99 cc., and the true measure becomes (15—0.99=) 14.01 cc., or practically 14 cc. This correction is applied throughout in constructing the following Urea Table, and thus a nearer approach to accuracy is attained, while the troublesome calculations are avoided.

Again, as each cc. of water displaced is equal to a cc. of nitrogen gas which displaced it, and this, when corrected for temperature represents 0.0027 gm. of urea, the number of cc. of water represents the number of times 0.0027 gm. of urea is contained in the 2 cc. of urine taken for the assay. But to obtain a percentage of urea it is a little easier to take the results from 1 cc. of urine and therefore the number of cc. of displaced water is divided by 2. Then the number so obtained multiplied by 0.0027 gives the percentage of urea in the urine. For example, suppose the displaced water from 2 cc. of urine taken be, after correction for temperature,

14 cc. This divided by 2 gives 7 cc. for each 1 cc. of urine. Then 7 times 0.0027 is 0.0189 gm. Then as this quantity of urea comes from 1 cc. of urine which is assumed to be 1 gm. although it is a little more, the quantity must be multiplied by 100 to give percentage, and this is the same thing as moving the decimal point two places to the right, and thus 0.189 gm. of urea becomes 1.89 per cent., and in this way the percentage column of the following table is obtained.

The first column of the table gives the reading from the measuring jar after having been corrected for 18° C. (64.4° F.) or 0° C. (32° F.). And the second column gives the percentage calculated upon the reading after being corrected for experimental temperature, and all the other columns are calculated from the corrected readings.

The third column gives the quantity of urea in grams contained in each measure of 500 cc. of the total urine of 24 hours' excretion, and the fourth column gives the quantity of urea in grams contained in each fluidounce of the total urine of 24 hours' excretion, both being only approximate because not [illegible] the temperature in measuring, and only for a fixed and [illegible] assumed difference in specific gravity between water and urine. The measuring jar of this apparatus is graduated with [illegible] degree of accuracy to half cubic centimetre up to [illegible] this measure of [illegible] fluidounce of water [illegible] accurately poured out. The fluidounce of the [illegible] specific gravity measure is [illegible] but when a measure [illegible] poured from a measuring glass [illegible] will remain in the [illegible] the measure to hold the quantity poured out [illegible] which [illegible] the difference between [illegible] and [illegible] [illegible] generally [illegible] assumed [illegible] 1. [illegible] specific gravity of urine is always greater than water [illegible] than a fluidounce of water [illegible] specific gravity must be considered and [illegible] compared with water as [illegible] and [illegible] grains and

these data are the bases for the calculations of the third and fourth columns.

The fifth column gives in gms. the quantity of urea in 473 cc. =1 pint of urine corresponding to each percentage result; and the sixth column gives in grains the quantity of urea in 1 pint of 16 fluidounces of urine, corresponding to each percentage result.

The seventh and eighth columns may not be useless for casual inspection. It has been estimated that the average normal excretion of urine in adults for each 24 hours is not far from 1181 cc., which is equal to 2.5 pints or 40 fluidounces, and the variation from this, above or below, is chiefly water. If, therefore, the excretion for 24 hours should be evaporated down to this quantity if above it, or be made up to it with water if below, and be then assayed for the proportion of urea, the results would be all that could be desired. Taking then 1181 cc. or 40 fluidounces., as an assumed standard, the seventh column gives in grams, and the eighth column gives in grains, the quantity of urea corresponding to each percentage that would be excreted in 24 hours. The estimated average normal amount may be 30 gms. equal to 462.96 grains, but "A range of from 20 to 40 gms. (308.6 to 617.2 grains) must at least be admitted in adults." (Tyson, edition of 1891.) It will therefore be seen that while the average normal excretion may be about 20 per cent. = 30.5 gms. = 471.2 grains, the range is a very wide one extending from 13 per cent. to 27 per cent. according to Tyson. This leaves only about one-third of the table below the lower limit of normal health, and the ninth column gives a probable indication of the limits consistent with ordinary health in adults.

It is hardly necessary to say that the table is one of approximative equivalents, and is read in horizontal lines.

One point should be always borne in mind in direct relation to any urea table, and that is, that all good authorities insist upon its being little more than a waste of time and labor to assay the urine of any particular hour of the day or night, and that unless a specimen of the total excretion of 24 hours can be had, the results are misleading and may be dangerously misleading. And farther that for the best results, and those which are most trustworthy, the assays of several successive days should be taken.

Table of Approximate Proportions of Urea in Urine [illegible]

One cubic centimeter of nitrogen gas at [illegible] C. [illegible] F. equals [illegible] urea.

Assumed room temperature for measurements 18° C. [illegible] F.

Rate of expansion [illegible] times the volume for each [illegible] applied for 18° C. [illegible] F. [illegible] 1 cc. as read off from the measuring [illegible] and the percentage [illegible] from the corrected reading.

Thirty cubic centimeters is assumed as equal to one fluidounce [illegible] verting any considerable quantities from one measure [illegible] cc. should be taken as 1 fluidounce.

In converting measures to weights and in using measures and weights together an assumed specific gravity for abnormal urine [illegible] 1.025 at 25° C. [illegible] F. and [illegible] cc. of urine of such sp. gr. weighs [illegible] gms. and 1 fluidounce weighs [illegible] grams.

Four hundred and seventy-three cubic centimeters is assumed as [illegible] one pint of sixteen fluidounces, and when these measures are used for urine they are assumed as weighing [illegible] and [illegible] grams respectively.

The seventh and eighth columns must not be taken as having [illegible] relation to or bearing upon the assay, excepting when the 24 hours' excretion amounts to [illegible] near to this measure, as the calculations are based upon [illegible] quantity.

[illegible]

REAGENTS.

The reagents for the estimation of urea by measuring the nitrogen which results from its decomposition, are, thus far, only two in number,—the hypochlorites and the hypobromites. These are chemicals whose nature is not very well understood and they are characterized by the condition that their elements are so loosely combined as to be, under all ordinary circumstances, in a state of continuous molecular change. That is, they are unstable combinations of their elements, and upon this quality their utility in this process seems to depend. But they are not equally unstable.

The hypochlorites are more stable, or change more slowly than the hypobromites, and therefore in this reaction for decomposing urea it is not necessary that they should be freshly made for each assay, or group of assays. But this characteristic which gives them this advantage involves the disadvantage that those of them which keep best are slowest in reaction with the urea, and give the longest and least definite end reaction. Both reagents with proper management decompose all the urea with evolution of all its nitrogen, and the quantity of urea decomposed is determined by the quantity of nitrogen evolved. Therefore, the object is so to manage the reagents as to decompose all the urea present, and to measure the nitrogen gas set free; and now the different management for the different ways in which the reagents are used, is to be considered.

USE OF THE HYPOCHLORITES.

One of the chief advantages that induced the writer to offer this apparatus and process in its original paper of 1884, was the facility given for its use by the easy access, almost everywhere, to the solution of chlorinated soda of the U. S. Pharmacopœia of 1870. This solution is essentially a solution of sodium hypochlorite and of sodium carbonate, bicarbonate and chloride, containing not less than 2 per cent. of available chlorine, and the change which it undergoes by keeping seems to be the slow conversion of the sodium hypochlorite into sodium chloride, wherein the chlorine is no longer available, and into free oxygen. This change is, however, so slow that bottles of it put up over 25 years ago with 2 per cent. of available chlorine, are in the writer's possession containing

0.6 per cent. of available chlorine, while freshly imported Labarraque's solution contains only 0.4 per cent.

The U. S. P. of 1880, however, changed the proportions of the ingredients, so that the solution of chlorinated soda is essentially a solution of sodium hypochlorite and chloride with very little or no sodium carbonate or bicarbonate, and containing not less than 2 per cent. of available chlorine (that is, of hypochlorite not yet changed into chloride). There has not yet been time for a long trial of the keeping properties of this solution of 1880, but the writer believes that it changes more rapidly than the solution of 1870. And that the solutions are very unlike is proved by the very singular fact, that although they have the same proportion of sodium hypochlorite, the one will completely decompose urea while the other will not. Then as the failure of the 1880 solution was apparently due to the absence of the excess of carbonic acid or carbonate of sodium present in the solution of 1870, as the only known difference in the formulas, carbonate of sodium was added to the solution of 1880, but with no influence upon its reaction with urea. But when proportions varying from 2 to 8 per cent. of sodium bicarbonate were added to the solution of 1880, it decomposed the urea perfectly, but gave traces of carbonic acid which became mixed in the evolved nitrogen, thus preventing its use in this way to render the 1880 solution available, although the readings [illegible] were [illegible] slightly too high. An [illegible]

and process also, of 1870, for the Pharmacopœia of 1890. Whether the Committee does or does not return to it, the writer will return to it in his own practice, and will send out no other than the 1870 solution. But as this solution will not be generally accessible while the 1880 solution will be, and as the 1880 solution will probably be continued in 1890, it is worth while to offer a formula and process for the extemporary preparation of the 1870 solution by which any physician, pharmacist or nurse can, in about three hours, make about 330 cc. or 11 fluidounces of the solution that will keep in good condition for a year.

EXTEMPORANEOUS SOLUTION OF CHLORINATED SODA.

Take of good Chlorinated Lime ("Chloride of Lime") 24 grams.
Sodium Carbonate ("common Washing Soda") 48 "
Water, a sufficient quantity.

Shake the lime salt very thoroughly with 200 cc. of water and pour the thinner portion of the mixture upon a wetted paper filter, receiving the filtrate in a 500 cc. bottle. Shake the residue of the lime salt with 75 cc. more of water, and when the first portion is nearly drained through the filter, pour on the whole of the second portion. When this has drained through, the clear filtrate should measure about 265 cc., and if the filter be a good one the time required will be about 2 hours. Dissolve the Sodium Carbonate in 90 cc. of hot water by agitation, pour the Solution into the bottle with the filtrate, shake well and filter. The filtrate should measure about 330 to 335 cc.

This extemporaneous solution of chlorinated soda is substantially that of the U. S. P. of 1870, and answers very well for this urea process, and when made from ordinarily good chlorinated lime or "Bleaching Powder," 10 cc. of the solution is quite sufficient for the reaction, and is better than a larger quantity. But if the lime salt be old and poor, or the solution be old, 15 cc. is a better quantity with which to charge bottle *A*; with this reagent a warm bath will shorten the process.

SOLUTIONS OF PURE UREA.

For trials with the various forms of these reagents in this apparatus and process, pure urea, well crystalized, was taken and its

freedom from moisture was proved by keeping it over sulphuric acid for 48 hours without appreciable loss. From this 2.5 per cent. and 2 per cent. solutions were freshly made every few days during the entire two months over which the trials extended, and when any considerable growths occured in the solutions they were not relied on.

CHLORINATED LIME, CHLORIDE OF LIME, OR BLEACHING POWDER

In "The Pharmaceutical Journal and Transactions," London, for March 29, 1890, Third Series, Vol. 20, page [illegible], Mr. [illegible] R. Dott, F. I. C., F. R. S. E., has a short paper, in which he recommends Solution of Chlorinated Lime for the assay of urea. He takes one part of Chlorinated Lime and three parts of water, and filters off the solution from the insoluble part. With this solution he fills a nitrometer, such as is figured in the Epitomes at page 1106, letting in the urine from the funnel, and getting very accurate results. A nitrometer is out of the reach of the ordinary physician and nurse, and not available for clinical use. But chlorinated lime is so largely used as a disinfectant that it is easily accessible of fair quality everywhere, and can be had without difficulty of the best quality and put up in glass for best keeping so that it is available and convenient for this apparatus if the quality can be depended upon. To test this point specimens in possession of the writer were tried for available chlorine, that is, chlorine in the condition of hypochlorite. These were all put up in amber glass and the bottles wrapped in paper.

No. 1 was put up about December 27, and then contained [illegible] per cent. available chlorine. Now, March [illegible], it contains [illegible] per cent. There was therefore an appreciable loss in about two months' keeping.

No. 2 was put up May [illegible], [illegible], and then contained [illegible] per cent. available chlorine. March [illegible] it assayed [illegible] per cent., and there [illegible] per cent. available chlorine [illegible] and [illegible] loss. At the present time [illegible] per cent. available chlorine.

[illegible]

pains being taken to get some of them from pharmacies of small business, where they would be likely to be oldest. All excepting No. 10 were put in either metal or pasteboard cylinders, well closed, containing one pound or half a pound each, and the cost, retail, was 15 to 20 cents per pound. All were put up by two dealers, but one of them sold two brands. The first 4 were put up by one party and the remainder by the other. One other brand, only, is known in this market, but it was not met with in buying the samples.

No.	3	contains	26.3%	of available chlorine.		Put up in	metal	cylinder.
"	4	"	26.2%	"	"	"	"	"
"	5	"	11.2%	"	"	"	"	"
"	6	"	35.4%	"	"	"	pasteboard	"
"	7	"	26.3%	"	"	"	metal	"
"	8	"	30.2%	"	"	"	pasteboard	"
"	9	"	36.4%	"	"	"	"	"
"	10	"	30.4%	"	"	"	paper parcel.	

Two grams from each of the five samples were successively put into bottle *A*, well shaken in the bottle with 10 cc. of water, and then used for the process with the 2 per cent. urea solution, but the results were only 1.72, 1.64, 1.51, 1.39 and 1.30 per cent., showing conclusively that the mixture without filtration would not answer for the process, although there is no known reason why it should not when the filtered solution answers well. Then from each of these ten samples 20 grams was weighed off and well shaken with 60 cc. of water in a measuring jar, and the mixture poured upon a paper filter in a funnel in a bottle marked at 100 cc. When drained the residue was washed on the filter until the filtrate measured 100 cc., and these solutions of chlorinated lime were kept for the process, each 10 cc. representing about 2 grams of each of the samples. Two assays were made with each solution, the first with 10 cc. representing 2 grams of the sample, and the second with 15 cc. representing 3 grams of the chlorinated lime of each sample.

The results were as follows, a 2 per cent. solution of pure urea being used.

No. 1	.2 gms	in 10 cc	sample containing	35% available chlorine gave	2.26
" 1	.3	" 15	" "	35	[illegible]
" 2	.2	" 10		[illegible]	[illegible]
" 2	.3	" 15	"	30	[illegible]
" 3	.2	" 10	" "	29.3	[illegible]
" 3	.3	" 15	" "	29.3	[illegible]
" 4	.2	" 10	" "	29.2	[illegible]
" 4	.3	15		29.2	[illegible]
5	.2	10	"	18.2	[illegible]
" 5	.3	" 15		18.2	[illegible]
" 6	.2	[illegible]	"	35.4	[illegible]
" 6	.3	15		35.4	[illegible]
7	.2	10	"	29.3	[illegible]
" 7	.3	15		29.3	[illegible]
8	.2	1		[illegible]	[illegible]
" 8	.3	15		[illegible]	[illegible]
" 9	.2	[illegible]		[illegible]	[illegible]
9	.3	15		[illegible]	[illegible]
10	.2	10		[illegible]	[illegible]
10	.3	[illegible]		[illegible]	[illegible]

That so many of these assays should come out so near to the actual percentage must be regarded as rather accidental, or partly the result of a steady room temperature, but when it is remembered that the skill of the writer's assistant in making the measurements is, after more than two months of almost continuous practice, much beyond that of the ordinary physician and nurse with limited practice, a part of the unexpected accuracy is explained. That the results should be so uniform with so great a difference in the quality of the chlorinated lime and in the quantity of the reagent taken may fairly be credited to the method, and it shows that chlorinated lime adapted to the method is very generally accessible. Ten [illegible] equal to 2 grams of the chlorinated lime [illegible] preferred [illegible] more prompt and complete and [illegible] [illegible]

the bottle causes slow expansion of the gases and air in the bottle *A*. About four assays can be made in an hour, but about 20 minutes of this time is taken in cooling bottle *A* four times to room temperature in the bath.

These solutions of chlorinated lime made as described above, may be taken as the first step in making the extemporaneous solutions of chlorinated soda, also previously described. If it was known that the solutions of chlorinated lime would keep well, and if they were accessible without the trouble of being made, solutions of chlorinated soda would be entirely unnecessary. But how long the lime solutions will keep is not known, but the great probability is that they deteriorate pretty rapidly, and are not trustworthy after a month's keeping. The soda solutions, however, keep very well for many months, and if they were accessible as they formerly were, the lime solutions would be entirely unnecessary. As it is, the lime solutions may be made as above directed, and be used for a short time most conveniently, and then what is left of such solutions can be converted into soda solutions very easily, as follows:

For every gram of chlorinated lime or 5 cc. of the lime solution take 2 grams of sodium carbonate, and dissolve this in 8 cc. of hot water by shaking in a bottle of double the capacity. To this solution add the lime solution, and shake the two well together. If the mixture gelatinizes at first set the bottle in warm water until it liquifies, and then having shaken well, pour the whole upon a paper filter. The filtrate will then be the extemporaneous solution of chlorinated soda of the U. S. P. of 1870, which will be effective in the process, and will keep well for months, or even for a year or more. Such solutions of chlorinated soda, made from the solution of chlorinated lime of the last series of trials, were used in the following series. But for a comparison of results the assays No. 1 are made from a chlorinated soda solution of the U. S. P. of 1870, that is now about 1 month old.

No. 1.	From chlorinated lime of		38	available	chlorine,	10 cc.	gave	2.14	from a	2%	solution.
" 1.	"	"	38	"	"	15	"	2.08	"	2	"
" 2.	"	"	26.3	"	"	10	"	2.14	"	2	"
" 2.	"	"	26.3	"	"	15	"	2.68	"	2	"
" 3.	"	"	18.2	"	"	10	"	2.02	"	2	"
" 3.	"	"	18.2	"	"	15	"	2.08	"	2	"

These trials show that the range of strength in the chlorinated lime from which the chlorinated soda is made, does not affect the

results so long as the variations in strength are within the limits of this set of observations, and therefore that any chlorinated lime likely to be found in the ordinary markets is as available for making solution of chlorinated soda for this process as it is for making solution of chlorinated lime for the process. In all these last trials the end reaction was slow, and therefore a warm water bath was used in every case, shortening the times of reaction to [illegible] minutes, or about the same as in the use of chlorinated lime solution.

SODIUM HYPOBROMITE AS A REAGENT

Sodium hypobromite has for many years been used and regarded as the standard reagent for the decomposition of urea, and when well managed it leaves nothing to be desired. Its chief disadvantages are that it must be recently made, and that this requires the keeping in readiness a strong solution of caustic soda and liquid bromine, both of which are irritant and corrosive agents, and free from danger when in hands not used to the management of such agents. This reagent is, however, as available for this apparatus and method as for any other, and its use has now to be [illegible].

SOLUTION OF CAUSTIC SODA

All authorities agree in advising 100 grams of caustic soda to be solved in 250 cc. of water, for this solution, and with these proportions the solution measures about 254 cc. and has a specific gravity at 15° C. (59° F.). This solution very soon corrodes a glass stopper in place, and soons destroys cork, so that it is best kept in bottles with rubber stoppers.

BROMINE

Bromine is found in the markets usually in small glass bottles with glass stoppers, and these are usually rather more than half full, and are still [illegible]. The stopper is carefully cemented in, and the bottle is well packed under the cover. The vials are then wrapped in paper and packed in whiting or chalk in the case. It stoppers [illegible] well put in they will leak, and if well put in [illegible] But with careful warming [illegible] stopper [illegible] experiments [illegible] have been used without [illegible] and only [illegible] weighed and measured as follows.

No.	1	contained	32.8 gms.,	which measured	about	11	cc.
"	2	"	25.9	"	"	8.5	"
"	3	"	28.7	"	"	9.5	"
"	4	"	15.7	"	"	5.5	" leaky.
"	5	"	29.0	"	"	10.0	"
"	6	"	29.6	"	"	10.3	"
"	7	"	29.9	"	"	10.3	"
"	8	"	24.7	"	"	8.3	"
"	9	"	29.1	"	"	10.0	"
"	10	"	24.3	"	"	8.3	"
"	11	"	30.4	"	"	10.4	"

One ounce avoirdupois is equal to 28.35 grams, so the average is a little short. A cc. of bromine at room temperature weighs about 2.942 grams.

THE REAGENT FOR USE.

Authorities advise that to the above solution of caustic soda, measuring 284 cc., 25 cc. of bromine be added, making 309 cc., and that the mixture be gently agitated until the bromine is dissolved. Then each cc. of this solution will contain about 9.354 grams of soda, and about 0.08 cc. of bromine, equal to about 0.235 gram of bromine. The ordinary direction for preparing the solution in small quantities is to take 10 cc. of the soda solution, and add 1 cc. of bromine to this, agitating gently till the bromine is dissolved. Then this quantity is all used for one assay, although greatly in excess, and it does not give as good results as smaller quantities.

This solution it is which does not keep well and therefore, has to be freshly made, but how long it will retain its efficiency for this reaction has not hitherto been determined. To test this point approximately it was found that 1.5 cc. of the freshly made solution was the smallest quantity that would completely decompose 2 cc. of a 2.5 per cent. solution of pure urea. Two days later, 3 cc. of the solution was the smallest quantity that would effect the same decomposition. Three days after the last result, 4 cc. was required to do the same work. Seven days later, 5.5 cc. was required. Four days later, 7 cc. was required. Twelve days later, 8.5 cc. was required. Nineteen days later, 13 cc. was required. Thus, after keeping for 47 days, more than eight times the quantity was required, indicating a rate of change that is not far from 0.24 cc. a day. But the quantities recommended to be taken for the assays are so greatly in excess of what is required, that if the recommendations be adhered to, the solution may be said to be effective for a longer time than 30 days. But it will be shown

later on that too great an excess is not only useless, but appears to be hurtful. As was stated above, it was found that [illegible] this solution when freshly made was as effective in decomposing the urea of 2 cc. of a 2 per cent. solution of urea as was a larger quantity, in this apparatus, and the results of the trials on this point are given below. The quantities of the solution used were in each case made up to 1 cc. by adding water, and each trial was repeated with the addition of 1 cc. more of water without perceptibly varying the result.

In No. [illegible]

[illegible]

These results, although fairly uniform, tend to confirm what was suspected in other trials, namely, that the great excess of this reagent tends to lower the result. This [illegible] be explained by supposing that the larger quantity [illegible] and water present dissolves and holds a larger proportion [illegible] trogen, leaving less to be measured, thus increasing the [illegible] error so that it is noticeable by this apparatus. In [illegible] parable to N[illegible] made with the apparatus of Pavy, [illegible] which he recommends [illegible] solution [illegible] of water [illegible] the decomposition [illegible] more than the proportion [illegible] gave only [illegible] per cent. In this case, the same quantity of reagent and water [illegible] [illegible] N[illegible] [illegible] Everything except the proportion [illegible] being the same [illegible] that gives [illegible] [illegible] gas [illegible] [illegible]

W[illegible] [illegible] and the greatest [illegible]

could not be ascertained, and the discrepancy must be charged to the imperfection of the apparatus.

THE REAGENT AS IMPROVED BY DR. RICE.

The time and trouble of preparing this solution frequently, and the risk of having it ineffective if kept, are very much lessened by a device suggested to the writer by Dr. Charles Rice, Chairman of the Committee of Final Revision of the U. S. Pharmacopœia. Dr. Rice dissolves the bromine in a solution of potassium bromide, and thus avoids the frequent handling of undiluted bromine. He uses the proportions of 125 gms. each of potassium bromide and bromine dissolved in water and made up to 1 liter or 1,000 cc. with water, and advises equal volumes of this and the soda solution to be mixed for use near the time of making the assays. This writer assumes, for theoretical reasons, to improve the formula by substituting sodium bromide for the potassium salt, and finds it answers the purpose a little better. Dr. Rice's procedure would then be as follows:

Take the contents of an ounce vial of bromine, whatever weight it might yield, say for example, 28.35 grams or an avoirdupois ounce, and an equal weight of sodium bromide. Having poured the bromine into a tared bottle of 500 cc. capacity, and taken the weight of bromine, add an equal weight of sodium bromide, and 100 cc. of water and agitate the mixture until the bromine is dissolved. Then add water until the solution measures as many cc. as eight times the number of grams of bromine taken. That is, if the bromine weighed 28.35 gms. the finished solution should measure ($28.35 \times 8 =$) 226.8 cc. Then equal volumes of this solution and the soda solution are mixed for the assay. This solution of bromine keeps indefinitely, so far as known, and is conveniently handled. It should be kept in bottles with glass or rubber stoppers. It contains 0.125 grams of bromine in each cc., and when mixed with an equal volume of the soda solution, the mixture will contain 0.0625 gm. of bromine in each cc. It is therefore but little more than one-fourth the bromine strength of the reagent as generally recommended for this use (0.0625 against 0.235 gm. in each cc.), yet for this reaction 5 cc. of it are equal to 4 cc. of the stronger solution, as is shown by the following trials. Each trial was made first with a solution in which potassium bromide was used as the solvent, and then with one in which sodium bromide

was used, but as there was no practical difference in the results only those with the sodium bromide are given. In each trial the soda solution and bromine solution were mixed in equal measures and made up to 100 cc. with water, excepting the first one where [illegible] cc. of each had 100 cc. of water added.

In No. [illegible] the use of [illegible] solution of urea with [illegible] gave [illegible]

In attempting to check some of the more important results of this paper by the use of the nitrometer as a more accurate instrument, it was found that the solutions of chlorinated soda were difficult to use with success because difficult to shake well [illegible] the results obtained by the use of the other reagents were [illegible] confirmed by the use of the nitrometer. Even the short results obtained from the extemporaneous solution of [illegible] cc. of soda solution and [illegible] of water for [illegible] per cent urea solution, that is, from the great excess of reagent, were confirmed by the nitrometer, the results in two trials [illegible] being [illegible] per cent.

ILLUSTRATION

It now only remains to give an example of the application of the method to urine.

An adult male in good health excreted [illegible] of urine. This urine was almost [illegible] of a good color, transparent and bright, and [illegible] test paper. Tests for albumen were tested by heat and [illegible] separately and together, and [illegible] specimen [illegible] Assuming the urea with solution [illegible] paper [illegible] with [illegible] and then with the [illegible] gave [illegible] and water [illegible] Referring this result to the test [illegible] [illegible] per cent [illegible] per cent [illegible] the nitrometer [illegible] [illegible] cc. [illegible] And this process [illegible] nitrometer has to be applied to

any other columns of the table that are required. The observer may use either grams or grains, or both, in interpreting his results, but only one is needed here to make the illustration understood. The 57 fluidounces of urine is 40 fluidounces from the seventh and eighth columns, plus 16 fluidounces from the fifth and sixth columns, plus 1 fluidounce from the third and fourth columns (40+16+1=57), and the figures obtained by the interpolation of the "In grains" columns are for 40 fluidounces, 271.20 grains,—for 16 fluidounces, 108.48 grains,—and for 1 fluidounce, 6.78 grains, and these added together give 386.46 grains as the total excretion of urea for the 57 fluidounces of urine in 24 hours.

On the day following, under similar conditions of diet and exercise, the same person excreted only 32 fluidounces of urine in the 24 hours. The first day had been clear, sharp and cold, with high barometer, and therefore the cutaneous transpiration had been low and the kidneys had to excrete the more water. The second day was warm and clear, with falling barometer, and with winter clothing on, the cutaneous transpiration was free, so that the kidneys had less to do. The 32 fluidounces of urine was of much deeper color and higher specific gravity (1.022), but in all other respects was like that of the preceding day. Assayed for urea in exactly the same way it gave 18 cc. of displaced water, indicating 2.27 per cent. of urea. Then 32 fluidounces being just 2 pints, is refered to column 6 ; and, the figures in grains multiplied by 2 give 339.52 grains as the total excretion of urea in the second period of 24 hours. Then 386.46 and 339.52 added together and divided by 2 give 362.99 grains as the average excretion of urea for two successive days. This is considerably below the assumed normal, but not inconsistent with good health.

CONCLUSIONS.

The conclusions reached by the work done in this paper may be usefully summed up as follows:

First, that the apparatus recommended is a convenient one for approximate results, and is fairly trustworthy within a total range of error of 0.3 per cent. or 0.15 per cent. on either side of the truth ; and that it does not require expert skill to attain these results by its use.

Second, that the apparatus and method are not confined to any

particular reagent for its best results, but may be used with any of those that have come within the scope of this paper.

Third, that the Solution of Chlorinated Soda of the U. S. P. of 1870, although not the best reagent for use, is much the most convenient, provided it can be bought ready made, simply because it is always at hand, keeps fairly well, and saves all the time and trouble of extemporaneous preparations.

Fourth, that the simple filtered solution of chlorinated lime is the best of all the reagents tried, while it gives the least trouble and requires least time in extemporaneous preparation, and the chlorinated lime from which to make it, is the most generally accessible of all the materials known to be applicable to this method.

Fifth, that the improved bromine process as used by Dr. [illegible], wherein the bromine is held in permanent solution by means of sodium or potassium bromide, is much the best way of applying the bromine reagent.

Sixth, that the ordinary way of using the bromine reagent, while it is no better than other reagents, if as good, involves the most trouble and risk of all, and cannot be recommended for inexpert hands.

Seventh, that all these reagents have been hitherto used in too great excess, not simply in wasteful excess, but also in [illegible] excess.

NOTES

Professor E. D. Campbell, in charge of the [illegible] and steel in the University of Michigan, suffered the loss of his sight by an explosion of gases on April 22, 1892. [illegible] As he was in the act of [illegible]

NEW BOOKS.

Blair's Water Analysis.*—Whoever Mr. Blair may be,—and it seems strange that with such a string of titles we should not know more of him,—he is either not an educated Englishman, or an exceedingly careless proof reader, as witness these sentences: "I gratefully acknowledge not only these suggestions of him" (Preface). "A dilute solution of ammonium chloride of the strength that each cc. contains" (p. 6). "And again with tap water till the drippings be neutral to litmus paper" (p. 7).

The author seems to be in ignorance of the fact that the Kjeldahl method had already been used for the analysis of potable waters (see preface). It has always seemed to the writer that too much valuable time has been given to finding quick methods for determining the amount of organic impurities in water,—results which when obtained could not be intelligently interpreted unless the nature of the water was already known by other tests,—best of all, by the test of actual use. What is wanted is a method for determining what *organisms* are contained in a water; of what nature they are, and how many are contained in a given volume. Such a method has lately been perfected, and will be published in this Journal.

Lindsay's Qualitative Analysis.†—This new edition of an old and well-known text-book needs little comment. Indeed, this is true of almost all books upon qualitative analysis, as the subject admits of very little variety of treatment. The metals are divided into seven groups: 1st, those precipitated by hydrochloric acid; 2d, those precipitated by hydrogen sulphid in acid solution, whose sulphids are soluble in alkaline solutions; 3d, those precipitated by hydrogen sulphid, but the sulphids insoluble in alkaline solutions; 4th, those precipitated by ammonia; 5th, those precipitated by ammonium sulphid; 6th, those precipitated by ammonium carbonate; and 7th, the remaining metals. There seems to be

*The Organic Analysis of Potable Waters. By J. A. Blair, M. B., C. M., D. Sc. Edin. L. R. C. P. Lond. Second edition. Phila. P. Blakiston, Son & Co. 1891.

†The Compendious Manual of Qualitative Chemical Analysis of C. W. Eliot & F. H. Storer, as revised by W. R. Nichols. Sixteenth edition. Newly revised by W. B. Lindsay, A. B., B. S., Professor of Chemistry in Dickinson College. New York: D. Van Nostrand & Co. 1892.

little that is new in the method of testing for acids. Part II contains directions for working with substances of unknown composition. The appendix which closes the book needs revision. For example, the author directs that common sulphuric, hydrochloric and nitric acids shall be used. Now these acids are usually, almost universally, very impure. The sulphuric generally contains iron, lead and arsenic. The hydrochloric contains arsenic, iron and chlorine, and often sodium sulphate and free sulpuric acid. The nitric almost invariably contains sodium sulphate, free sulphuric acid and chlorine. Such directions are of little consequence where the teacher is competent and knows better, but where, as is often the case in so called high schools, the teacher's knowledge is obtained entirely from the book, the results are not encouraging. The old fashioned form of blower for blast-lamps is figured on page 176. Fletcher's form is certainly preferable.

Brown's Assaying.* The third edition of this book was reviewed in this Journal, Vol. III, p. 464. In this fourth edition a considerable amount of new material has been added, the book now containing 533 pages. The chapter on "Lead Ores" has been rewritten. To the appendix, chapters upon the "Tin Assay" and "Gold and Silver Ores," and a short chapter on the "Determination of the Specific Gravity of Minerals" have been added. To fit the manual for the English market, the values are also given in English money.

*Manual of Assaying [illegible] Silver [illegible] Minerals. With an [illegible] and [illegible] [illegible] By Walter [illegible] Brown, B.S. [illegible] Philadelphia: Lippincott & Co. [illegible] J. H. Sargent & Co. [illegible]

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NOTES ON THE DETERMINATION OF PHOSPHORUS BY NEUTRALIZATION OF "THE YELLOW PRECIPITATE."*

BY DR. M. ROTHBERG AND W. A. AUCHINVOLE.

Some years ago F. Hundeshagen (*Zeit. anal. Chem.* **28**,141–172) advanced the opinion that phosphomolybdate of ammonium may be titrated with caustic soda. A synopsis of his method is as follows:

The "yellow precipitate" is washed with neutral ammonium nitrate and dissolved in warm, dilute ammonia, excess of ammonia expelled by evaporation, and nitric acid added to re-form the yellow precipitate. After again evaporating, to decompose ammonium nitrate, raising the temperature finally to 180°, the dish is cooled, and a measured amount of caustic soda added. After stirring until all is in solution, the excess of alkali is found by titrating back with standard nitric acid, using phenolphthalein as an indicator. 1 cc. of $\frac{n}{10}$ soda equals 0.00061739 gm. of phosphoric anhydride.

In the JOUR. ANAL. AND APPLIED CHEM. for February, 1892, Mr. C. E. Manby gives, practically, the same method as the result of his own independent investigation.

Without again going over the ground so well covered by Mr. Manby's paper, we will give the results of our experiments, thanking Mr. Manby for valuable suggestions.

The method as it stood was too long to be called a "rapid" method, and after a few experiments we found that good results could be obtained by titrating the "yellow precipitate" directly, without previous re-precipitation, with the advantage that it shortened the method by at least one-half.

From the results of our experiments, we are led to believe that only with extreme care is it possible to obtain good results with

*This article was received before the article by J. O. Handy in the April No. had been published.—Ed.

the evaporation method, and in making a run of forty to fifty phosphorus determinations per day, as we usually do, some modification was necessary if we wished to use the method.

DETAILS

Take 1 to 2 gms. of steel, according as the phosphorus is high or low, put in a 12 oz. Erlenmeyer flask, add 15 to 20 cc. nitric acid, 1.20 sp. gr.; as soon as violent action ceases, put on the lamp, bring to a boil, oxidize with permanganate, dissolve the precipitated manganese dioxid with sugar or ferrous sulphate, boil one minute longer, cool to about 40° C., add 50 cc. of molybdate solution, shake for one minute, stand in a warm place for five minutes, and then filter, using a 7 cm. S. & S. N. 590 filter; rinse out the flask with one per cent. nitric acid, and wash four times on the filter with the same, then wash five times with potassium nitrate (3 gms. per liter), to remove free nitric acid.

Transfer paper and precipitate to a 8 oz. beaker, add from a burette enough standard soda to dissolve the precipitate, dilute to 50 cc. with water, add 2 drops of phenolphthalein, and titrate at once with a standard solution of nitric acid.

As the compound formed by dissolving the "yellow precipitate" in caustic soda is very volatile, it is essential that the titration be made promptly.

If the solutions are of such strength that 1 cc. alkali equals 1 cc. acid, and 1 gm. of steel is taken for a determination, then the combined alkali in cc. × .0123 = per cent. phosphorus, if it is assumed that N/10 solutions are used.

We have verified our work by gravimetric methods, and the results agree closely. In a steel in which Booth, Garrett & Blair found .05 P., we found .04 .05.

We will say in regard to running our standards, that we treat them in the same manner as our daily work, taking a standard in the dish, same, and titrating all exactly the same.

We believe that no errors are likely to be introduced in using the [illegible] Emmerton's method, or in washing the yellow precipitate.

As to the reaction which takes place when caustic soda is added to the "yellow precipitate," we can say it is a very interesting

study, which we hope to treat in another paper. For the present we will simply say, "when just enough caustic soda is added to dissolve the precipitate, and the solution is evaporated spontaneously over sulphuric acid, it shows white efflorescent crystals, easily soluble in hot or cold water."

LABORATORY CAMBRIA IRON CO.,
JOHNSTOWN, PA.

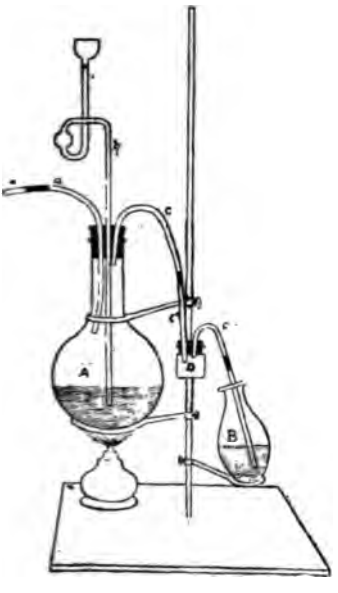
THE DETERMINATION OF SULFUR IN IRON AND STEEL.

BY ABRAM T. EASTWICK

Place 3 gms. of drillings in a pint flask *A*, and close it with a rubber cork fitted with funnel tube and delivery tube *c*, and tube *a*.

Similarly close bottle *D* with cork fitted with tube *c'* and *c''*; connect *c* and *c'*.

To flask *B*, which should be about one-half the size of *A*, add 15 cc. of an ammoniacal cadmium chlorid solution and dilute with 100 cc. of water. Insert a glass tube in *B*, and connect it with *c''*.



Fill tube *b* with dilute hydrochloric acid (equal parts acid and water), and blow through *a* to be sure of no leak. Replace cap *a'*, and add to flask *A* 80 cc. of dilute hydrochloric acid.

Boil the solution until the drillings are dissolved. When no more gases are evolved at *B*, remove the flame and blow through *a* to drive over any evolved gases still remaining in *A* and *D*. Leave *a* uncapped and disconnect *c''* from the tube in *B*.

All the sulfur generated in *A* is now contained in *B* as cadmium chlorid. Any hydrochloric acid distilled over will remain in *D*.

Now add to *B* a few cc. of starch water (allowing the tube to remain in the flask, as some cadmium sulfid is apt to adhere to

it), acidulate with strong hydrochloric acid, and immediately titrate with a standardized iodin solution. Agitate the contents of the flask just before titrating, in order to insure a complete solution of the cadmium sulfid.

An ordinary retort stand is a convenient support for the apparatus; a small sample bottle answers the purpose for *D*.

Cadmium Chlorid Solution.—Dissolve 120 gms. of pure cadmium chlorid in cold water, and add [illegible] of strong ammonia. If the cadmium chlorid contains any impurities insoluble in the ammoniacal solution, they should be filtered, and the solution kept in a tightly stoppered bottle.

Iodin Solution.—Dissolve [illegible] gms. of iodin [illegible] gms. potassium iodid in [illegible] of water and dilute [illegible]. Keep the solution in a dark place and tightly corked.

It is unnecessary to describe the method for standardizing the iodin solution here, as it is described in text-books [illegible] *Elementary Chemical Analysis*, [illegible] p. [illegible]. The strength of the solution must be carefully determined, however, as [illegible] generally contains impurities which, of course, makes the solution weaker than its theoretical strength.

A rapid and convenient method of standardizing the [illegible] solution is by the use of drillings, in which the sulfur has been accurately determined. The known per cent of sulfur is divided by the number of cc. of solution required, divided by the number of gms. of drillings used, is the strength of iodin solution.

The method described here is essentially the Cadmium method [illegible]. But I find that if the intervening bottle [illegible] between the generating and receiving flasks [illegible] [illegible] with the drillings are being dissolved. This [illegible] large quantities of [illegible] solution [illegible] sulfid [illegible] being filtered off from the [illegible] immediately titrated. [illegible] have frequently checked by [illegible] checked by Bunsen Gas

rett & Blair, and others. They have always agreed to .004 per cent. or less.

It must not be forgotten, in connection with this or any evolution method, that in the case of pig-iron some sulfur is liable to remain in the insoluble carbonaceous residue, which should always be examined when absolute accuracy is required. In technical analyses, however, the carbonaceous residue is not generally examined for pig-iron of ordinary composition, as it rarely retains more than a very small proportion of the total sulfur in the iron; but this is a matter best left to the individual judgment, for great diversity of opinion seems to exist as to the necessity of examining such residues.

ON LABORATORY VENTILATION.

By Charles F. Mabery.

The chemical laboratory has become an important feature in the various departments of higher education and an indispensable adjunct in scientific training. Instead of buildings or rooms of moderate size, within ten years the rapidly increasing classes in chemistry in colleges and schools of science have rendered necessary buildings and even rooms large enough to accommodate comfortably several hundred persons. It is a familiar fact that the atmosphere of a laboratory has a well-established reputation for odors that are not especially agreeable to persons unaccustomed to them. That the ordinary smells and odors in a well ventilated laboratory are not unhealthful, is well attested by the unimpaired health of instructors who have spent a large portion of their lives in such atmospheres. With a moderate number of persons at work in a laboratory room of suitable size, it is a matter of no especial difficulty to carry away the deleterious gases without contaminating the general atmosphere. But with larger classes general ventilation, which includes complete removal of injurious gases simultaneously with sufficient renewal of the atmosphere of the room to keep it in good condition, presents features that require careful consideration. It must be distinctly understood at the outset that proper ventilation of such a room requires two systems operating independently, and at the same time to a certain extent in conjunction with each other.

For removal of harmful gases heavier than air, such as hydrogen sulfid, the gaseous products of the solution of metals in [illegible] or sulfuric acid, which must be generated in an enclosed space shut off from the general atmosphere of the room, a powerful upward draught is necessary. Such a draught may be maintained in tall flues provided a sufficient difference in temperature exists in the hoods and in the flues, and this is usually accomplished by some such means as a gas jet placed at the opening [illegible], or upward currents are produced by forcing air into the hoods. Independent of the strong draughts upon which the hood ventilation depends, the general ventilation requires a constant [illegible] circulation, which is established in part by the large number of lamps usually burning at the desks, especially if there are [illegible] openings at the base of the room and in the ceiling. With the aid of forced air currents sent in through flues at the base, the circulation may be accelerated to any desired extent.

Moreover, in some localities, and Cleveland is one of them, with certain directions of the wind occasionally there are strong downward currents that are troublesome, and these [illegible] be controlled by counter pressure. The introduction of fresh air under pressure is more advantageous than through windows, since it can be easily controlled, and open windows not only interfere with lamp flames, but the direct draughts are dangerous, especially in the heated condition of the laboratory atmosphere [illegible]. While [illegible] the laboratories [illegible] in the large building [illegible] for these [illegible] [illegible]

[illegible]

of the building with the exit flues. All these flues are constructed in the two cross walls enclosing the main hall, which is thirteen feet wide. Each flue has a terra cotta lining 8 x 12 in., with the lower opening 7 ft. from the floor, and they are brought together above the fourth floor into four larger flues *b*, each 36 x 21 in., which begin on the fourth floor. On the fifth floor each of the larger flues has an opening 21 x 48 in., closed by an iron door, and opposite each door is a steam radiator of 30 ft. radiating surface, heavily coated with asphalt paint. The radiators have automatic air vents, and they are attached to a separate steam pipe with a valve in the basement. Two flues entering the left main flue *b*, plate *A*, in a cross wall are not shown in the section. As a part of the general ventilation, the lecture room has six openings at the base leading into flues that extend to the basement for connection with the blast pipe, and a register in the ceiling 20 x 24 in. opening into the large flue *a*, section *A*. The general laboratory has five flue registers at the base, and the ceiling openings enter the escape flues *a*, the larger (36 x 30 in.) containing on the fifth floor a capacious tin-lined copper box for supplying distilled water from condensed steam. Four flue registers are also set at the base of the quantitative laboratory on the first floor, and the ceiling opening is at the base of the larger flue *a*, plate *B*. The dotted line at the left of this flue represents the position of the smoke flue leading from the boiler room. The tops of these flues are 80 ft. from the basement floor.

The air blast is given by a Buffalo pressure blower capable of delivering any desired volume of air below 2,800 cubic feet per minute. It is set so as to take air from outside the building, and in cold weather to send it through a chamber containing a steam coil. The motive power is obtained by means of a three kilo-watt Edison Motor, and attached to the same counter-shaft is a small high pressure blower to supply an air blast for lamps and furnaces. Through the generosity of the Cleveland Electric Power Co., an electric current of about 500 volts is taken from their street main. The advantage of four large flues is evident from the operation of the system; with a smaller number it would be difficult, if not impossible, to carry gases so far against strong winds blowing in the opposite direction. In its efficiency and the slight care that it

requires, this method of ventilation is in all respects satis
In every hood flue there is a strong upward draught.

At my suggestion, Dr. A. W. Smith, Assistant Profe
Analytical Chemistry, kindly determined with an anemom
velocity of the currents just within the hood flues at th
openings. His results confirm the more general observatio
cerning the circulation within the hoods. The diminished
in the hood flues that are extended farthest from a vertica
tion to the main flues, verifies in a striking manner the adv
of four large flues alluded to above. With the hood w
raised six inches, each test was continued five minutes
following table the serial numbers correspond to those of th
as shown in the sections. One set of observations was ma
the blower in operation and the second set without it. Th
on the hood ventilation of a slight pressure in the room
perceptible.

No. of Flue	Velocity in Feet per	
	With Blower	W
	Without Blower	W
Plate A		
4 Preparation Room		
6 Lecture Room		
7 Organic Laboratory		
Plate B		
1 General Laboratory	[illegible]	
5 " "	[illegible]	
7 " "	[illegible]	
9 "	[illegible]	
6 Quantitative Laboratory Steam Hood	[illegible]	
8 General Hood	[illegible]	
12 "	[illegible]	

These tests were made May 14, when the atmosphere w
most unfavorable condition for satisfactory ventilation
rainy weather had prevailed for nearly a week, with an un
low barometric pressure.

To determine with some precision the influence of inadequa
ventilation upon the atmosphere of a large laboratory, samples
air were collected and analyzed by Mr. M. B. Punnett, a stu
chemistry. With the exhausting ventilators closed, one sam

9
12
10

was collected near the ceiling and another (2) at the level of the working tables. Calling this set of samples (*a*), a second set (*b*) was collected at the same point with the ceiling ventilators open and the base registers closed. A third set (*c*) was collected with the system in full operation, the blower delivering 1200 cu. ft. of air per minute. This room is 57x38 ft. and 16 ft. high. The samples were collected when the room was occupied by 65 persons with lamps burning freely throughout the room, and the condition of the atmosphere is shown by determinations of CO_2, which gave the following results:

Parts of CO_2 in 10,000.

	a.		*b.*		*c.*		
1.	1	2	1	2	1	2	2
CO_2	23.68	23.23	16.95	15.40	9.15	8.13	8.17

For the sake of comparison, carbon dioxid was determined in the lecture room with the base registers closed and the ceiling register open after it had been occupied 45 minutes by 50 persons. The samples collected near the outer wall contained 9.99 parts CO_2 in 10,000, and a second sample collected near the interior wall contained 11.47 parts CO_2. In analysis of the atmosphere outside the building, Professor Smith found 4.42 parts CO_2.

The operation of this system of ventilation as it is demonstrated by the circulation in the different parts and by the composition of the atmosphere under varied conditions shows clearly that upward circulation assisted by pressure is the simplest and the most efficient means for adequate renewal of the air, at least in a chemical laboratory. Between such a system, and one frequently in use in which the vitiated air is allowed to rise to the ceiling and is then drawn downward through base openings, the essential difference is that in the first the air is in its best condition in all the lower parts of the room, while in the second the air in such portions of the room as are near the base openings is always vitiated.

I desire to acknowledge my obligations to the architect, Mr. F. S. Barnum, for the efficient aid he has rendered in the construction of the details of this system, especially in the general ventilation of the building.

CHEMICAL LABORATORY OF THE
CASE SCHOOL OF APPLIED SCIENCE,
May 17, 1892.

A MICROSCOPIC SEDIMENT COLLECTOR

By Porter W. Shafer, Iowa City, Ia.

The minutely divided solid matter held in suspension by liquids is usually examined under the microscope either by placing a drop of the liquid under a cover glass, or by allowing the sediment to subside to the bottom of a conical glass vessel and then by means of a glass tube removing a drop of the sediment for examination. The suspended matter is, however, usually so sparsely disseminated that the former method is not practicable. It therefore becomes necessary to concentrate the sediment. The method of concentration by settling in a conical vessel has disadvantages which it may be well to enumerate briefly.

1st. Some kinds of suspended matter by reason either of their extremely minute state of division or because their specific gravities are nearly the same as, or less, than that of the liquid settle very slowly or not at all.

2d. When the suspended matter has the power of independent motion, as much of the microscopic life of water, it remains in suspension.

3d. By reason of the different sizes, specific gravities and other qualities of the various elements that make up the suspended matters, the sediment does not settle uniformly. Some elements float, and others remain upon the sloping sides of the vessel. These escape examination. The sediment at the bottom, instead of being uniform, is apt to be in stratified strata. The elements which subside most rapidly are at the bottom, and the lighter elements may be deposited more or less regularly above it. When examining such a deposit, some of this obtained we may be sure that all the different kinds of suspended matter are represented, or still less can we be sure that all the elements are represented in the exact proportions in which they exist in the [illegible]

[illegible] water [illegible] the [illegible] the water [illegible] [illegible] When [illegible] [illegible] [illegible]

A recent method of concentrating and enumerating the larger organisms (diatoms, algae, etc.) is the Sedgwick-Rafter method, devised and used in the laboratory of the Massachusetts State Board of Health. In this method a measured amount of the water is filtered through a plug of sand of suitable fineness and purity. The larger organisms remain upon the sand. Bacteria and disease germs pass through the sand and escape the examination. The sand is removed from the funnel and agitated with a measured small bulk of water. The sand sinks promptly, leaving the larger organisms in suspension. A measured small part of this water is then placed in a special cell, and the organisms are counted under the microscope by use of a device in the eye-piece which restricts the field of view to a small square of known dimensions. (Mass. State Board of Health, Report on Purification of Sewage and Water, 1890, pp. 799–811.)

Now it occurred to me that if *all* the suspended matter (including bacteria and disease germs) in a measured amount of water could be brought upon an ordinary cover-glass or slide, unmixed with any filtering medium or other foreign matter, it would give both a qualitative and quantitative exactness to the microscopic examination of sediments. For this purpose I have devised the apparatus figured herewith. (U. S. Pat. 474,267.)

The apparatus is shown in section in Figs. 1 and 2. Fig. 1 shows the arrangement for depositing the sediment upon a cover-glass. Fig. 2 is an arrangement for deposition upon a slide. *A* is a graduated glass tube 5 inches long and ¾ inch in internal diameter, open at both ends, and ground off square. The base of the tube is 2½ inches in diameter. The filter *B* and cover-glass *C* are, for the purpose of better illustration, exaggerated in size; *D* is a pile of blotting paper, cut in sizes about 2½ inches square; *E* is a glass vessel; *F* is a brass base; and *G* is a spring whose object is to press the filter tube firmly in contact with the mass of blotting paper. The pressure may be graduated by means of the links of the chain *H*.

In Fig. 2, *J* is a sponge which takes the place of the blotting pad in Fig. 1; *I* is a glass slide; *K* is a loose glass cover. In operation, the liquid is slowly drawn off in the direction of the arrows by the capillary attraction of the bibulous material, while the sus-

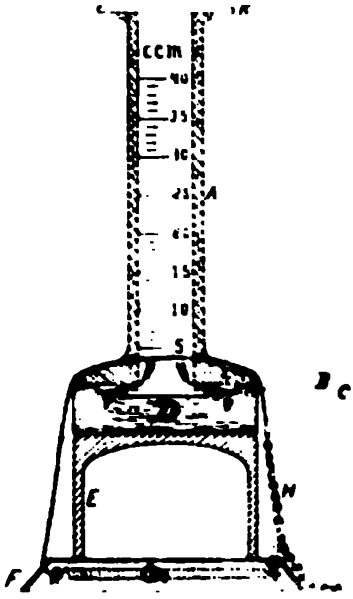


Fig 1

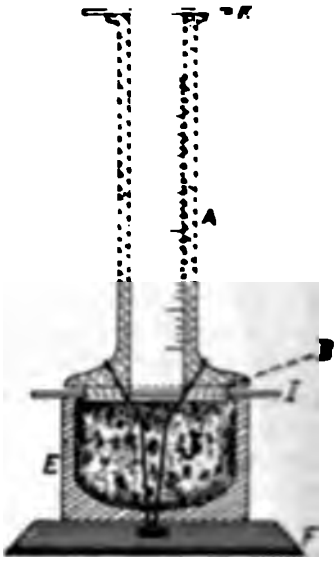


Fig. 2

pended matter remains conveniently deposited upon the [illegible] glass.

Everything depends upon the rate of filtration [illegible] the material of the filter and pressure of the spring [illegible] that [illegible] of water requires [illegible] the larger [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] deposited instead of the

upon the cover-glass or upon the slide. The cover-glass is perhaps preferable. The apparatus is shown in Fig. 1. Take a piece of No. 2 Swedish filter paper about two inches in diameter and make an aperture in the centre of it ¾ inch in diameter. This is the filter. Make it thoroughly wet and place it evenly over the aperture at the base of the tube. Place a well cleaned one-inch cover-glass evenly over the opening in the filter. It will adhere to the wet filter. Moisten the top piece of the pad of blotting paper and replace it. Place the top of the tube through the loop; bring down the tube carefully upon the blotting pad so as not to displace the cover-glass. Then pull down and fasten a link of the chain when the desired pressure has been attained. The apparatus is now ready for filtration.

Shake up the sample of water in a glass vessel. Then, by means of a pipette, which is moved about while the water is being drawn in, take out a sample of water and place it in the tube until the desired amount is obtained. It is not possible to get even moderately agreeing results from the same bottle of water when the water is shaken and poured into the filter tube. The suspended matter does not remain uniformly distributed through the liquid during the act of pouring. Cover the tube with a glass slip and set it aside, merely taking note of the beginning and end of the filtration.

In experimenting on the water of the Delaware river, it was found that all enumerations of the larger organisms agreed fairly well when the time of filtration of 25 cc. was over three hours. When 25 cc. required two days or more, bacteria were found in abundance upon the cover-glass. In general, it may be said, that the more minute the object sought for, the slower the filtration must be.

Dr. A. L. Kotz, in experimenting with the apparatus upon a sample of cistern water that had caused a local epidemic of typhoid fever, found that when 10 cc. filtered in 20 hours, he obtained no typhoid bacilli in the deposit. When, however, 5 cc. required 3 days, the characteristic bacillus was found in abundance. Dr. Kotz was afterwards able to confirm the results of this direct examination by succeeding in the preparation of pure cultures of typhoid bacilli from the water.

When the filtration is ended, the larger organisms are found uniformly distributed over the cover glass. When the filtration has been too rapid, the organisms are more abundant near the edge of the deposit. The method of enumeration of the larger organisms was as follows. The deposit on the cover glass was [illegible] inch in diameter. For the examination a one-tenth inch [illegible] and [illegible] eye piece were used, and the tube was drawn out [illegible] a point that the field of view was exactly [illegible] in diameter as measured by a micrometer. The deposit, being [illegible] inch in diameter, contains [illegible] fields. By counting the organisms in a large number of fields taken at random, the average number in each field is easily obtained. This multiplied by the whole number of fields gives the total number of organisms in the [illegible] taken from which the number in each cubic centimeter is [illegible] calculated.

In the matter of sampling, it was soon found that [illegible] any number of organisms could be obtained from the same [illegible] simply varying the speed of flow. When the water [illegible] the hydrant in a slow smooth stream there were comparatively few organisms. When the water was turned on full, the number was very large, because of the stirring up of the sediment in the pipe by the rapid current of water. The following [illegible] organisms [illegible] in four samples of [illegible] water were made, and the [illegible] with [illegible] from May [illegible]. The smaller [illegible] were [illegible] when the water was [illegible] a slow [illegible] when the water was turned on full.

The results, 192 in sample C, and 44 in sample D, show that filtration is too rapid when only one hour is required. Allowing an average of 300 of these larger organisms to each cubic centimeter, we take in, in an ordinary glass of water of 200 cc., about 60000 of them. It is fortunate that these do not belong to the harmful class of micro-organisms.

If desired, the sediment may be deposited upon the slide instead of upon the cover-glass, as shown in Fig. 2. The perforated filter (2 x 3 in.) is saturated with water, and the glass slide is laid down upon it so that the aperture in the filter is exactly in the middle of the slide. The ends of the filter are then folded over the back of the slide. The slide is laid over the mouth of the vessel, which contains a sponge which has been wet and well squeezed out. The sponge must press against the bottom of the filter The slide and filter may also be laid upon the blotting pad as in filtration upon the cover-glass.

For the examination of stagnant water, it is well to use a cell just large enough to fall within the rim of the tube. Examinations carried on in this way are vastly more interesting than by the usual way of placing a single drop under the cover-glass. The apparatus enables us to crowd all the life of many hundred drops under one cover-glass, and a more interesting sight it is not possible to imagine. In this way I was enabled to crowd a slide with the beautiful Volvox Globator to such an extent that I had the pleasure of seeing 90 individuals in the various stages of their life history in one field of view.

DETECTION AND ISOLATION OF TYPHOID BACILLI IN CISTERN WATER.

By A. L. Kotz, M. D.

The following notes are the record of a bacteriological examination of a cistern water, consumed by two families, in which six members were attacked with typhoid fever, and two died.

The water for analysis was collected in a sterilized Erlenmeyer flask, from the spout of a chain pump, after the water had been kept running about five minutes. It had a slight ochre color, but was perfectly transparent. About one hour after the water was collected, four gelatine culture plates were prepared of it; two with

0.25 cc., and two with 0.50 cc. each. The colonies were [illegible] on the fourth day. The variation in the number [illegible] on the different plates, proportionately, was very slight [illegible] gave an average of 2003 micro-organisms per cubic centimeter. [illegible] account of the large number of organisms, and especially [illegible] a saprophytic nature it was impossible to isolate the [illegible] present by the usual method. Cover glass preparations [illegible] water, prepared with Mr. P. W. Shimer's filtering apparatus [illegible] scribed in the preceding paper, revealed a large variety [illegible] among which was one presenting the characteristic morphological appearance of the typhoid bacillus. Further culture [illegible] with a fresh sample of the water diluted with sterile [illegible] tilled water, gave better results. In this way eight different species were isolated; of these six were saprophytes [illegible] pathogenic. The method of Chantemesse and Widal [illegible] zing the culture medium, was also employed. To [illegible] nutrient gelatine five to ten drops of a 5 per cent solution [illegible] lactic acid were added. By this process perfectly pure [illegible] typhoid bacilli were obtained. The above examinations were carefully carried out in every detail. But it will be seen that the method ordinarily employed to isolate the typhoid bacillus [illegible] in this case, and that of Chantemesse and Widal [illegible] Every one familiar with bacteriology of water knows [illegible] the difficulty caused by the presence of a large number [illegible] plete organisms. Water contaminated with typhoid [illegible] [illegible] of the typhoid [illegible] from this difficulty [illegible] [illegible] the typhoid [illegible] [illegible] results with [illegible]

[illegible]

water, in the shortest possible time. By using moistened and sterilized manila paper for the filter (which answers best for this purpose) one cubic centimeter of water will pass through the apparatus in about 24 hours and leave the organisms evenly distributed over the cover glass. In case pathogenic germs are found, the water may safely be condemned until the results of culture tests become known.

CHANGES OF METHODS OF ANALYSES BY THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

[FROM THE LABORATORY OF BREYER AND SCHWEITZER, 159 FRONT ST., N. Y.]

The methods of analyses of agricultural products, as laid down by the Association of Official Agricultural Chemists, are applied by many chemists who do not belong to that learned society. Some use these methods because the original literature is not accessible to them; others, especially those connected with the fertilizer trade, because they are compelled to follow those directions, very often against their better knowledge, in order to obtain analytical results, conformed to those obtained in the State Agricultural Experimental Stations.

These methods being published by the authority of the Secretary of Agriculture, and thus having the appearance of official approval, it ought to be supposed that there always must be only the best of reasons to warrant any change in a method once adopted, which has the sanction of chemists of the highest standing. Therefore it is difficult to understand how the chemists assembled in the lecture-hall of the Columbian University of Washington, on August 14, 1891, could have assented to the proposition of Wm. C. Stubbs, Ph. D., Audubon Park, New Orleans, La., to change the figure 144 in Clerget's formula (Bulletin **31**, p. 76) to 142, 4. Anyone proposing such a change in a formula which is used by all the chemists in the sugar-industry, and is approved by the highest authorities, is at least supposed to be well versed in the appertaining literature and to be possessed of sufficient penetration to discover the difference between the conditions to which the figures 142.4 and 144 respectively apply. For the first, time this change was proposed in the "Sugar-Cane," Vol. **22**, No. 246, p.

32, by some sugar-polarizators. To this one of us answered in "Sugar-Cane" Vol. 22, No. 248, p. 158. We assume that the "Sugar Cane" is not in the hands of all the readers of this paper and we therefore quote as follows:

CLERGET'S METHOD OF INVERSION

To the Editor of "The Sugar Cane":

Sir: In Number 240, January 1890, of "The Sugar Cane" [illegible] report of the Committee of the Louisiana Sugar Chemists' Association [illegible] "Methods of Chemical Analysis," describing experiments executed for the purpose of finding "the correct expression of the formula used in correcting [illegible] Clerget's method of inversion" and to test the correctness of the [illegible] figure of 142.4, "the inaccuracy of results obtained by the use of Clerget's original constant of 144 having become apparent." In the [illegible] article the Committee recommend "the use of the constant 142.4 in [illegible] determinations hereafter." From the description of the experiments executed, and the results obtained by such experiments, and [illegible] sion derived from said results, it appears clearly that the experiments have been faithfully executed, and that the authors of the report are [illegible] with the literature appertaining to the subject. The above [illegible] will embarrass and mislead those, who like those using polarizators [illegible] sugar plantations, etc., have not the knowledge and skill to test [illegible] methods themselves. But who may still be in a position to apply Clerget's method of inversion, and it will give rise to doubts as to the [illegible] said method with chemists who are not conversant with the [illegible] This is the reason which induces me to make a few remarks [illegible] point out the inaccuracies contained therein. In the report [illegible] that a normal solution of sucrose which polarized [illegible] only 99 when read at a temperature of [illegible] [illegible] It is well known that the specific rotation of sucrose is affected by variations of temperature. [illegible] [illegible]

were certainly too low (too low left hand rotation) for some reason, of course unknown to me, the authors of the report conclude: "These results would appear to confirm very fully the correctness of the constant 142.4 as obtained by Landolt." And thereby, without much ado, is condemned a method and a formula recommended, tested, and retested by chemists of high standing and authority. The above results of the Committee, however, do not by any means confirm the correctness of Landolt's constant. This 142.4 found by the Committee is not the 142.4 found by Landolt, as Landolt determined his 142.4 for a solution containing one-half normal weight of saccharose in 100 cc. and not like the Committee, for a solution containing one-half normal weight of saccharose in 55 cc. Gubb and others having shown that the rotatory power of invert sugar solutions increases with the concentration of the solution and the amount of acid employed for the inversion, the difference between Landolt's 142.4 (and Creydt's 142, and Herzfeld's 142.66) and Clerget's 144 is easily explained. There is, therefore, no need to change Clerget's original constant and formula (except, perhaps, for Tuchschmid's revised formula), as Clerget's method and formula gives for all practical purposes sufficiently reliable results, provided the inversion, polarization, and reading of temperature are executed with care and skill. I am fully aware of the well-founded objections raised against Clerget's method of inversion —against the use of the German half normal weight—while Clerget used the French half normal weight—against the concentration of the acid, &c., —but still the application of the constant 142.4 for the calculation of the results, obtained by polarising sugar solutions, inverted accordingly to Clerget, will cause a far greater error than all the other weak points of the method taken together.

Yours, &c.,

THEODOR BREYER.

New York City, 110 Front Street.

It is surprising, to say the least, that after this publication such a method should be proposed and accepted as a standard, and we take occasion to once more call attention to its glaring defects, to prove the necessity of an analyst's league against the rash conclusions of a minority making the rules as at present.

Another proof of the dangers of these changes is the determination of potassium by Lindo, as changed by Gladding in 1885. After seven years standing, Mr. Winton now discovers (*Bull* **31**, p. 148) that the use of chloride of sodium in the Lindo-Gladding method is not necessary. Every chemist with average knowledge must have seen, immediately after the Gladding method was introduced how weak and unscientific are the reasons for the use of chloride of sodium.

We are now collecting material, and are already in possession

of figures, which prove that this method is [illegible] able, and that the determinations made after Lunge-[illegible] necessarily give erroneous results. We will publish [illegible] of our research at an early date.

AN IMPROVED METHOD OF DETERMINING SMALL PERCENTAGES OF SILVER AND GOLD IN BASE METALS, MATTES, ETC.

[illegible]

Any one having frequent occasion to report the [illegible] and gold in such material as crude copper, copper matte, [illegible] metals, iron, zinc, etc., will appreciate the advantages [illegible] which affords accurate results with little expenditure [illegible]. The large production of pure copper by electrolysis [illegible] silver and gold bearing copper ores renders some [illegible] very desirable in view of the various transfers [illegible] smelters, [illegible] mattes to the refiners, and last the [illegible] the electrolytic refinery, in which transfers [illegible] and charge of the bullion contents.

While the proposed method is [illegible] [illegible] temperature, the silver and gold contents in [illegible] mattes resulting from [illegible] copper [illegible] [illegible] the method of silver [illegible] [illegible] [illegible]

[illegible]

much copper, or is hard or brittle, it is scorified with the addition of more test lead if necessary. When the lead button is soft and of proper size, it is cupelled and the button weighed and parted. Several scorifications are sometimes necessary before the button is ready for the cupel.

The two objections to this method are, first, the loss of silver during scorification and cupellation, the latter due chiefly to the copper remaining in the lead which it is practically impossible to remove in the scorifier, and which takes silver into the cupel. These losses I found to amount to from 2.33 to 2.78 per cent. of the silver present in the copper. My experiments were made with pure copper and pure silver, the silver being added in the proportion of 100 ounces per ton alloy.

The second objection is the small amount of bullion which can be operated upon, which necessitates the use of many scorifiers where small amounts of gold are to be estimated, which is usually the case.

To avoid the doubtful results of scorification processes, the following method has been adopted at the copper works of a firm having large interests at stake:

One assay ton of copper is dissolved in nitric acid, diluted, and allowed twenty-four hours to settle. The solution is now filtered from the slight sediment containing the gold. A few drops of hydrochloric acid are added to the filtrate, and the solution again allowed twenty-four hours for silver chloride to deposit, when it is filtered, and washed, and the two filters dried, combined, scorified with test lead, and cupelled. The chief objections to this are, (1) the time required; (2) the small amount of precipitate obtained, and the danger of loss in scorifying silver chloride; (3) the greater solubility of silver chloride as compared with the bromide.

While the method used at these works is an advance over previous practice, yet the time employed and the uncertainties indicated leave much to be desired. The protracted time allowed for settling is necessitated by the exceedingly fine condition of the gold resulting from the solution of a metal carrying possibly from .10 to 5 ounces of gold per ton of metal. It would pass through a filter unless allowed to aggregate by standing.

The larger quantity (to say 100 ounces of silver per ton) will

give but a slowly subsiding cloud impossible to filter when newly precipitated as chloride. The scorification of these combined precipitates, one of them being silver chloride, cannot give results quite satisfactory, despite the time involved, some [illegible] eight hours at least.

The method which I will now briefly describe was devised to meet just such cases, and is suitable for the bullion [illegible] of zinc, iron, nickel, etc., as well as the sulphides and arsenides of iron and copper. To illustrate the proposed method which has been found effective and useful, the treatment is detailed for a crude metallic copper carrying both silver and gold. It will be understood that sodium bromide is chosen as a precipitant because of the greater insolubility of silver bromide over the chloride, and also that the soluble lead salt is added in order that the heavy precipitate of lead bromide may envelop and promptly carry down the silver bromide cloud which otherwise would require long waiting for its subsidence, as well as to furnish the lead necessary for cupellation.

Weigh out from one to four a[illegible], depending upon its [illegible], place it in a beaker of [illegible] capacity, and add gradually enough acid to dissolve it completely; heat until red fumes cease [illegible] off; dilute with water and add [illegible] grams of lead acetate [illegible] and when dissolved, add [illegible] dilute sulphuric acid and allow the lead sulphate to settle. Filter into a [illegible] flask, fill to the mark with distilled water.

The filter contains the gold which has been collected and carried down by the sulphate of lead. The filter paper and precipitate are dried, the paper burned, and the ash and lead sulphate scorified with test lead. The button is cupelled, and the gold, with any trace of silver it may contain, is weighed. Add silver and part the gold in the usual way. Note the amount [illegible] and find the proportionate amount which [illegible] the solution [illegible] to be desired.

In order that there may be [illegible] the solution [illegible] equal parts [illegible] which is saturated [illegible] stirring as long as a precipitate appears. The precipitates settle quickly and [illegible] and wash with cold water; [illegible] should be used, and the washing be

continued until the washings are free from copper. Any bromide of lead dissolved during the washing, may be neglected, as I have never found it to contain more than a trace of silver, even when assaying ores carrying many thousand ounces.

The precipitate when dry can be brushed from the paper without difficulty, and thus the trouble of burning the filter is avoided.

The bromides are now mixed with three times their weight of carbonate of soda and a small amount of flour or other reducing agent, placed in a small crucible covered with borax glass, and melted down in the muffle. The button should weigh about 2 gms., and be free from copper and other injurious impurities. This button is cupelled at a low temperature, so that the cupel "feathers" nicely. The time required is from three to five minutes. Duplicate assays usually agree within two-tenths of an ounce per ton.

The following examples are from copper bullion:

	Oz. Silver.	Oz. Silver.	Oz. Gold.
No. 1	61.30	61.20	.10
No. 2	63.45	63.30	.17

Had the gold button contained silver, one-half of its silver contents would have been added to the silver recovered from the solutions, since the gold is estimated on the whole weight, while two determinations of silver are made on the same weight.

The following is an example from a silver-bearing cast-iron from the U. S. Mint at Philadelphia. It was dissolved in nitric acid, diluted, and precipitated with lead and sodium bromide. After washing, the bromides were dried and brushed from the filter. No. 1 was mixed with 10 gms. of litharge, a little flour, the usual amount of soda, and covered with borax. Melted down and cupelled, the button gave 30.80 ounces per ton. No. 2 was mixed with test lead and borax and scorified. It gave 29.90 ounces per ton, .90 of an ounce less than No. 1. However, this would be considered a very close agreement by the old method.

The following is an ore from Colorado, very base, and with a gangue of sulphate of barium. It proved very unsatisfactory to assay by scorification, duplicates not agreeing at all. The ore was treated with nitric acid and filtered, the residue being assayed separately.

The following are my results:

	No. 1 Oz.	No. 2 Oz.
Residues	[illegible]	[illegible]
Solutions	[illegible]	[illegible]
As a total	[illegible]	[illegible]
Difference of	[illegible]	

Gold was not separated in the residues. The highest assay gotten by scorification was about 467 ounces, which shows [illegible] ounces in favor of the new method, with a reasonably close agreement in different assays.

CONTRIBUTION FROM THE CHEMICAL LABORATORY U. S. DEPARTMENT OF AGRICULTURE.

XXIV. NOTE ON A QUALITIVE TEST FOR STRONTIUM IN THE PRESENCE OF CALCIUM.*

By K. F. McEllroy and W. D. Bigelow.

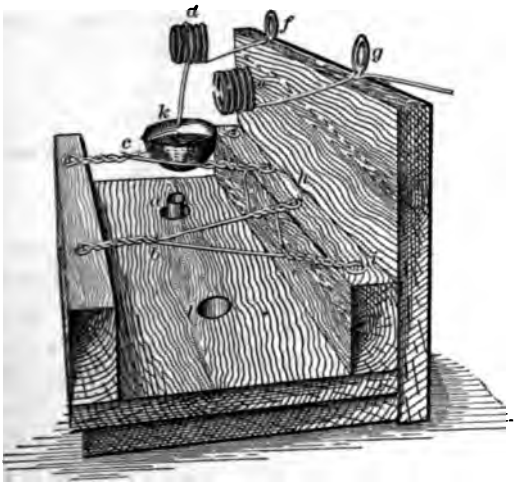
If a mixture of carbonates of strontium and calcium, such as is obtained in the ordinary course of analysis, is dissolved in hydrochloric acid, the solution evaporated to crystallization on the water bath and the residue taken up by dilute acetone (1 part of acetone by volume to 1 part of water), yellow chromate of potassium likewise dissolved in 50 per cent acetone and made alkaline by a drop of ammonia, when added to the liquid at once throws down anhydrous chromate of strontium. After a lapse of about ten minutes no strontium can be detected by sulphuric acid in the filtrate from this precipitate. Calcium is not precipitated, but after some hours a few crystals of the chromate may form. The strontium chromate is a fine mealy precipitate, filtering with great ease. It is intended to make an attempt to use this as a quantitive reaction, and some few determinations have been made and have given fair results. It is difficult, however, to secure commercial calcium salts which are free from strontium and vice versa. Dilute alcohol and methyl alcohol act in much the same way as acetone, but do not effect the separation so satisfactorily. Since making the above experiments we have received a number of the [illegible] containing an abstract of some work done by W. [illegible] and F. Reppert on a similar separation of calcium and strontium chromates in dilute alcohol. They have found the method is not quantitive. As they stated, we [illegible] found acetone preferable.

* [illegible]

FRAME FOR ELECTROLYTIC DETERMINATIONS.

By G. H. Meeker.

This frame is designed to unite convenience in handling the dishes and positive electrodes, ease in brightening the contacts, and such simplicity in make and material as will render it easily set up from what is at hand in nearly all laboratories.



It consists of a wire triangle to support the platinum dish, and a coil of wire to hold the positive electrode in position—both the triangle and the coil being supported by a suitable frame of wood, as shown in the cut. An auger hole may be bored in the bottom of the frame directly beneath the triangle to admit the tube of a Bunsen lamp for furnishing heat in cases where it is desired to precipitate the metal from a hot solution.

The frame figured above was made from an old 50 lb. bichromate box. It is 15 inches long, 6 inches high, and 6½ inches wide. The long pieces which support the triangles are made of ⅝ inch, and the rest of the woodwork of ¾ inch material. The triangles, *b* and *c*, and the coils, *d* and *e*, are made of No. 11 copper wire (or any fairly heavy wire). The triangle can be made in one piece, but it is easier, perhaps, to make it by twisting together three equal lengths of wire. The only disadvantage in using three pieces is that by oxidation the contact may possibly become poor. Each side of the triangle measures 2½ inches inside the twist. The coils are made by wrapping the wire spirally around a piece of glass tubing, and then sliding it off. One end of the wire must remain long enough to attach to the back of the frame, so as to be held just over the triangle.

The triangles are tacked to the frame, as shown in the illustration, and connected electrically with each other. The connecting wire is best soldered to the triangle to insure good contact, but this is not imperative. The coils are also connected by a wire and fastened to the frame by screws or nails. The cut shows two screw-eyes used for this purpose.

In operation the dishes are set on the triangles and the platinum rods are thrust between two adjacent turns of the coils. The coils will be found to be very convenient, and taking, as they do, the place of binding screws, are the feature of the appliance.

Both the triangles and the coils are easily brightened, to make good contact, by rubbing with a piece of emery paper.

LAFAYETTE COLLEGE
CHEMICAL LABORATORY

ATOMIC WEIGHTS

EDITED BY F. W. CLARKE

Oxygen. — The gravimetric composition of water has been investigated by Dittmar & Henderson, by the old method of synthesis over copper oxide. The authors begin by a careful review of the earlier determinations by Dumas and Erdmann and Marchand, and point out various sources of error. They find, for example, that when hydrogen is dried by means of sulphuric acid it becomes contaminated by traces of sulphur dioxide.

After many preliminary experiments they give a series of fourteen syntheses, of which one, No. 4, was lost. The results of the thirteen are as follows:

No.	Experiment	H	O
1	Reduced	[illegible]	[illegible]
2		[illegible]	[illegible]
3		[illegible]	[illegible]
5		[illegible]	[illegible]
6		[illegible]	[illegible]
7		[illegible]	[illegible]
8	Reduced	[illegible]	[illegible]
9	Reduced	[illegible]	[illegible]
10		[illegible]	[illegible]
11		[illegible]	[illegible]
12		[illegible]	[illegible]
13		[illegible]	[illegible]
14		[illegible]	[illegible]

The last column is not given by the authors, but is calculated here for better comparison with other data. Experiments 6, 8, 2, are rejected by Dittmar and Henderson because of irregularities. The ten remaining figures give, in mean, H = 1.009133 ; ± .00029. Experiments 7, 9, 10, 11, 12, 13, 14, proceeded with the most regularity, and are therefore entitled to the most confidence. Their mean is H = 1.00882 ; ± .00030. Corrected for a small amount of hydrogen occluded by the copper, this mean becomes 1.00848, or O = 15.866, when H = 1.—*Proc. Phil. Soc. Glasgow, v.* **22**, *1890–'91, p. 33.*

By Lord Rayleigh the density ratio H : O has been thoroughly redetermined, with all necessary corrections. In mean, from 11 weighings of O and 19 of H, the final result is :

H : O : : 1 : 15.882.

The last figure, corrected by Morley's data for the composition of water by volume, gives for the atomic weight of oxygen, O = 15.880.—*Proc. Roy Soc., v.* **50**, *April, 1892.*

Boron.—Atomic weight redetermined by J. L. Hoskyns-Abrahall, who titrated the bromide, BBr_3, with a standard solution of silver.

In mean, six concordant experiments give B = 10.816 ; ± .0055, when Ag = 107.923 and Br = 79.951.—*Proc. Chem. Soc., April 20, 1892.*

AN APPARATUS FOR DETERMINING THE LIABILITY OF OILS TO SPONTANEOUS COMBUSTION.*

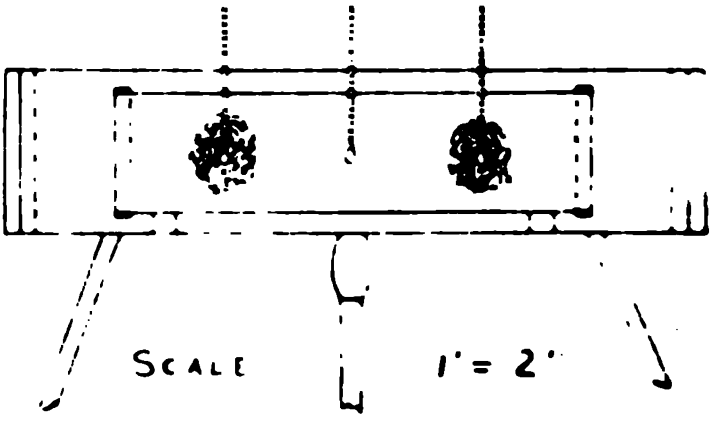
By Ellen H. Richards.

In 1877-79 the New England Cotton Manufacturers' Association and the Boston Manufacturers' Mutual Fire Insurance Company took up the question of the conditions under which the oxidation of oils, dye-stuffs, etc., in contact with easily inflammable materials, such as cotton in bales, cotton waste, rags, etc., was most likely to occur, with a view to better protecting themselves from loss and to insure a more efficient inspection. The problem was submitted to Prof. Ordway, of the Institute of Technology, who suggested a form of laboratory apparatus to experimentally determine the facility with which oils oxidize under favorable conditions. From the results of the investigations of Mr. William B. Albright,

*From the Technology Quarterly, Dec. 1891.

Class of '77, and Mr. Frederick W. Clark, Class of [illegible] was perfected which has been used by me ever since in determining all test cases which have come up in connection with the Insurance Company. The first general conclusions were stated by Professor Ordway, under whose direction the experiments were carried on, in the Proceedings of the New England Cotton Manufacturers' Association, October [illegible] 1878, No. [illegible]. The final report was made December 1, 1884, in Special Report No. [illegible] Boston Manufacturers' Mutual Fire Insurance Company.

The requirements of an apparatus for laboratory use [illegible] too large, safe for use in an ordinary room, enabling a test to be made in a working day of eight hours, easily managed and [illegible]ble of giving uniform and reliable results, are fulfilled in the one shown in the following sketch.



The apparatus consists of [illegible] weight [illegible] [illegible]

burner placed midway between the ends. The entire apparatus may be inclosed in a shield if the place is draughty. The diameter of the inner tube permits the use of fifty grams of cotton waste (such as is used to clean machinery), to which is added an equal weight, fifty grams, of the oil to be tested. The oil is evenly distributed by careful manipulation, the waste rolled compactly but not too tightly, and pushed into the end of the tube, which it should fill so that gentle pressure is required to move it. The bulb of the thermometer is now carefully inserted into the middle of this ball. The metal cover, which should fit loosely so as to admit a little air, but affording protection from currents, is put on, and then the outer cover of wood. A blank of unoiled waste is placed under the same conditions at the other end. The thermometer in this blank should not be permitted to rise above 100° or 101° C. at the most. To have it reach this temperature, the thermometer must be kept at about 125°. Since the balls of waste are equidistant from the source of heat, the necessary conditions are fulfilled if there are no draughts to blow the flame or cool one end of the cylinder.

In this apparatus anything which can be finely divided—shavings, leather, skeins of dyed yarn or rolls of dyed cloth—may be readily tested. Paper pulp, boards, and other carbonizable substances may be tested at a higher degree of heat for inflammability. Coal has not been subjected to experiment in it.

The results of greatest practical value obtained in the use of this apparatus have been, first determining the cause of fires; and second, determining the degree of safety of the various oils used in manufacturing. Mineral oil, as is well known, is not liable to spontaneous combustion; and a certain percentage of animal or vegetable oil may be added to mineral oil without materially increasing the danger under ordinary circumstances. This percentage varies according to the oil; with neat's-foot and first quality lard oil some 50 to 60 per cent. may be used. With cotton-seed, not over 25 per cent. is allowable. The claim so often made for so-called "safe" oils, said to have been changed by special and secret processes of refining so as to be no longer dangerous, is easily exposed by this test.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
February, 1892.

WATER ANALYSIS

Table Showing the Number of Grains per U.S. Gallon [illegible] and [illegible] corresponding [illegible] Milligrams per Litre

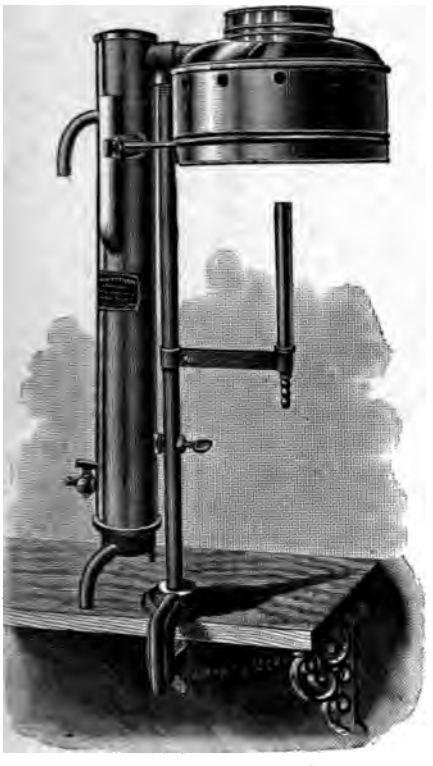
BY [illegible] B. STEERMAN

Milligrammes per Litre	Grains per Imperial Gallon	Grains per U.S. Gallon	Milligrammes per Litre	Grains per Imperial Gallon	Grains per U.S. Gallon
1	[illegible]	[illegible]	51	[illegible]	[illegible]
2	[illegible]	[illegible]	52	[illegible]	[illegible]
3	[illegible]	[illegible]	53	[illegible]	[illegible]
4	[illegible]	[illegible]	54	[illegible]	[illegible]
5	[illegible]	[illegible]	55	[illegible]	[illegible]
6	[illegible]	[illegible]	56	[illegible]	[illegible]
7	[illegible]	[illegible]	57	[illegible]	[illegible]
8	[illegible]	[illegible]	58	[illegible]	[illegible]
9	[illegible]	[illegible]	59	[illegible]	[illegible]
10	[illegible]	[illegible]	60	[illegible]	[illegible]
11	[illegible]	[illegible]	61	[illegible]	[illegible]
12	[illegible]	[illegible]	62	[illegible]	[illegible]
13	[illegible]	[illegible]	63	[illegible]	[illegible]
14	[illegible]	[illegible]	64	[illegible]	[illegible]
15	[illegible]	[illegible]	65	[illegible]	[illegible]
16	[illegible]	[illegible]	66	[illegible]	[illegible]
17	[illegible]	[illegible]	67	[illegible]	[illegible]
18	[illegible]	[illegible]	68	[illegible]	[illegible]
19	[illegible]	[illegible]	69	[illegible]	[illegible]
20	[illegible]	[illegible]	70	[illegible]	[illegible]
21	[illegible]	[illegible]	71	[illegible]	[illegible]
22	[illegible]	[illegible]	72	[illegible]	[illegible]
23	[illegible]	[illegible]	73	[illegible]	[illegible]
24	[illegible]	[illegible]	74	[illegible]	[illegible]
25	[illegible]	[illegible]	75	[illegible]	[illegible]
26	[illegible]	[illegible]	76	[illegible]	[illegible]
27	[illegible]	[illegible]	77	[illegible]	[illegible]
28	[illegible]	[illegible]	78	[illegible]	[illegible]
29	[illegible]	[illegible]	79	[illegible]	[illegible]
30	[illegible]	[illegible]	80	[illegible]	[illegible]
31	[illegible]	[illegible]	81	[illegible]	[illegible]
32	[illegible]	[illegible]	82	[illegible]	[illegible]
33	[illegible]	[illegible]	83	[illegible]	[illegible]
34	[illegible]	[illegible]	84	[illegible]	[illegible]
35	[illegible]	[illegible]	85	[illegible]	[illegible]
36	[illegible]	[illegible]	86	[illegible]	[illegible]
37	[illegible]	[illegible]	87	[illegible]	[illegible]
38	[illegible]	[illegible]	88	[illegible]	[illegible]
39	[illegible]	[illegible]	89	[illegible]	[illegible]
40	[illegible]	[illegible]	90	[illegible]	[illegible]
41	[illegible]	[illegible]	91	[illegible]	[illegible]
42	[illegible]	[illegible]	92	[illegible]	[illegible]
43	[illegible]	[illegible]	93	[illegible]	[illegible]
44	[illegible]	[illegible]	94	[illegible]	[illegible]
45	[illegible]	[illegible]	95	[illegible]	[illegible]
46	[illegible]	[illegible]	96	[illegible]	[illegible]
47	[illegible]	[illegible]	97	[illegible]	[illegible]
48	[illegible]	[illegible]	98	[illegible]	[illegible]
49	[illegible]	[illegible]	99	[illegible]	[illegible]
50	[illegible]	[illegible]	100	[illegible]	[illegible]

AN AUTOMATIC WATER STILL.

By G. W. James.

To those using distilled water this automatic water still will be found both convenient and economical; being self-regulating, does not require attention when in use, and it also has the advantage of being easily cleaned. The retort has a well fitted cap which can be removed to admit the hand. The water supply pipe to the retort is provided with a screw cap at the elbow, which allows both tubes to be cleaned. The inner tube of the condenser can be taken out by unscrewing same, making all parts of the apparatus accessible. The retort and condenser revolve on the iron support, and any scale or deposit may be removed without unfastening the clamp. It is well made of heavy copper, tin-lined throughout.



TO OPERATE THE STILL.

Connect the stop-cock to the water supply by means of rubber tubing. Attach sufficient rubber tubing to the overflow (upper bent) pipe to conduct the cooling water to a sink or waste pipe. Turn on the water so that it flows out at the overflow tube, sufficient to keep the condenser cool. Gas connection to Bunsen burner can be made with rubber tubing. The still is so arranged that the water in the retort is maintained at a constant level, and being small in quantity, is quickly heated to boiling; the steam is condensed and delivered from the distilled water outlet (lower bent)

tube. The quantity produced exceeds one half gallon per [illegible]. This apparatus fitted with burner for gasoline or [illegible] gas, may also be obtained. Both forms are supplied [illegible] ards & Co., Chicago and New York.

NOTES UPON THE ESTIMATION OF CHLORINE IN ELECTROLYZED SOLUTIONS.[1]

[illegible]

The numerous experiments made during the last few years upon the production of chlorine, hypochlorites and chlorates by the electrolysis of solutions of chlorides, have brought into the [illegible] of analysts solutions containing chlorine in several [illegible].

It has been found that rapid volumetric methods for the determination of the combinations in which the chlorine exists are a necessity where such solutions were to be [illegible] and the writer thinks that a description of the methods [illegible] employed, which they contain little that is new, may be [illegible] to chemists who deal with similar problems.

By the direct electrolysis of aqueous solutions of [illegible] chloride at ordinary temperatures, solutions are [illegible] contain sodium chloride, sodium hypochlorite and [illegible] and this general action is modified by the [illegible] chlorides. A most complex case is that [illegible] one of sodium chloride, in which this property [illegible] the temperature is raised to [illegible] C. the solution [illegible] mixture of hypochlorite and sodium chlorate.

Such solutions may be very [illegible] examined by the methods described below.

ESTIMATION OF CHLORINE COMPOUNDS AS [illegible]

A [illegible] the solution [illegible] with [illegible] the [illegible] process.

[illegible]

[illegible]

[illegible]

the quantity of chlorine combined as hypochlorite may be calculated.

ESTIMATION OF CHLORINE COMBINED AS CHLORIDE.

The portion of the original solution which has been titrated with sodium arsenite is now conveniently made up to a known volume and an aliquot part is taken. To this part a solution of pure potassium chromate is added, and the solution then titrated with silver nitrate of known strength. The presence of arsenic compounds does not interfere with this titration in any way; in fact, sodium arsenite may be used as an indicator in the place of potassium chromate, and equally good results may be thus obtained.

The figures furnished by the titration with silver solution give the chlorine present as chloride and hypochlorite together in the original liquid. By subtracting the chlorine combined as hypochlorite from the chlorine shown by the titration with silver solution, the chlorine present per cubic centimeter as chloride is readily obtained.

ESTIMATION OF THE TOTAL CHLORINE.

It might seem at first thought that the total chlorine could be obtained by the titration of the original solution which had been electrolyzed; but this is not the case, as during the electrolysis of a chloride solution there is a decrease in its volume caused by the rise in temperature due to the current, so that the contents per cubic centimeter of the solution before and after electrolyzing are not comparable, unless, in the latter case, the solution is carefully brought to its original volume by the addition of water. A further error is unavoidably introduced by a loss of chlorine due to its escape directly into the air during the electrolysis, a loss which the writer has always observed in the various forms of apparatus which he has used.

As the solutions under discussion contain chlorine in two oxidized forms as well as in the form of chloride, it is of course evident that for the determination of the total chlorine the simplest method will be the reduction of the oxidized chlorine compounds to the form of chloride, and a subsequent titration with silver solution. Various reducing agents have been recommended from time to time for the reduction of chlorates to chlorides with a view

to the subsequent titration of the chlorides with silver solution. After many experiments the writer has found that the most satisfactory agent for this reduction is a saturated aqueous solution of sulphurous acid. This was suggested by Rose, and lately Engel has called attention to its possible use in this connection. Chlorates are completely reduced to chlorides by boiling for a few moments with an excess of an aqueous solution of sulphurous acid with or without the addition of nitric or sulphuric acid. Thus the following figures were obtained in the analysis of a sample of commercial chlorate of potash by reduction with sulphurous acid solution, after acidifying strongly with nitric acid, boiling off the excess of sulphurous acid, followed by titration with silver solution in the manner to be mentioned below.

	Theory for pure $KClO_3$	Found			
Chlorine	28.93	[illegible]	[illegible]	[illegible]	[illegible]

As during the reduction free acid is formed in the chlorate solution, even if it is not added at the beginning, the use of potassium chromate as an indicator, together with direct titration with silver nitrate solution, failed to give satisfactory results. The figures obtained, however, were entirely satisfactory if the reduced solution was treated with an excess of silver nitrate solution of known strength, ferric alum added as an indicator, and the excess of silver nitrate determined by titration with ammonium sulphocyanate solution in the manner recommended by Volhard.

The total chlorine being thus obtained, the [illegible] chlorate [illegible] is easily found by [illegible] the total quantity the [illegible] previously ascertained [illegible] in the form of [illegible] and hypochlorite.

It [illegible]

The writer has used still another method which gives good results, but it is less rapid than those mentioned. After the determination of the hypochlorite and chloride present has been made, the total oxidizing power of the original solution, due to the hypochlorite and chlorate contained in it, may be estimated by adding a known quantity to an excess of an acid ferrous solution, containing a known quantity of ferrous sulphate, boiling for a few moments in an atmosphere of carbonic acid, and titrating the unoxidized ferrous salt with potassium permanganate or potassium bichromate. The oxidizing power of the original solution can be calculated from the ferrous iron oxidized by it; and as the hypochlorite present is known, the chlorate present can be calculated.

ABSORPTION OF CHLORINE.

In testing the efficiency of electrolytic chlorine generators it is most convenient to absorb the chlorine produced in sodium hydrate solution. The amount of chlorine already present in the alkaline solution should be determined by a preliminary analysis. The alkaline solution which absorbs the chlorine will contain it mainly as hypochlorite, but also as chloride and chlorate. A known fraction of the absorbing liquid is taken, made up to 1,000 cc., and of this 50 cc. are measured and 20 cc. of sulphurous acid solution and 5 cc. of nitric acid added, the sulphurous acid removed by boiling, and the the total chlorine is then easily found by the method described for the estimation of the total chlorine in the electrolyzed solution, and from this the chlorine originally in the solution must be subtracted.

I see no reasons why the methods given above may not be applicable to the analysis of bleaching powder in cases where the estimation of total chlorine and chloride is desirable.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
February, 1892.

SEPARATION OF ARSENIC, ANTIMONY, AND TIN.*

BY JOHN CLARK, PH. D.

About a year ago (*Jour. Soc. Chem. Indust.*, **10**, 444) I pointed out that arsenic could be estimated in alloys and minerals by means of ferric chloride; and I have now to lay before the Society the

*Jour. Chem. Soc. [Lond.], May, 1892.

experiment which I have made to extend the use of ferric chloride to the separation of arsenic, antimony, and tin. With this object I prepared solutions of arsenious acid, antimony trichloride, and stannic chloride of known strength, and perhaps it is right that I should state that the strength of the antimony solution was determined by precipitating the metal as sulphide and drying the precipitate at 130°. For this investigation I have assumed that the trisulphide of antimony, dried at 130°, is pure Sb_2S_3. In my experiments, the above mentioned solutions were mixed in various proportions, and, in order to imitate closely the conditions in which these metals are obtained in the ordinary course of a chemical analysis, the mixed solutions, in every case where the arsenic was estimated, were, in the first place, precipitated with sulphureted hydrogen, and the precipitate washed with water. The mixed sulphides, while still moist, were then removed from the filter by piercing the bottom and washed into a distillation flask with 50 per cent. HCl (sp. gr. 1.15). Any traces still adhering to the filter were extracted by boiling with a little dilute caustic soda. When the filter is not separated from the precipitate, the paper is disintegrated and charred in the process of distillation, and some dark colored organic compound is formed which interferes with the correct separation of the tin from the antimony.

Process.—After the addition of the alkaline liquid with which the filter has been treated, an excess of ferric chloride, followed by a strong hydrochloric acid, is added to the distillate in the flask. The solution which I used for this purpose was made by dissolving 1 part of solid ferric chloride in [illegible] parts of water, [illegible] chloride and by sodium [illegible] which quantity employed contained [illegible] parts of iron in the form of chloride for each part of tin and antimony. The flask is then connected with a spiral glass condenser, the end of which [illegible] water and [illegible] [illegible] The contents of the flask are [illegible] [illegible] At the end of the

third distillation, under these circumstances, the whole of the arsenic will have passed over into the condenser. The presence of arsenic is generally indicated during the distillation by the appearance of more or less of a yellow precipitate in the distillate and in the tube of the condenser. This precipitate consists of a mixture of sulphide of arsenic and sulphur, and is due to a little chloride of sulphur which distills off along with the chloride of arsenic, and, in contact with water, is decomposed into hydrogen chloride and thiosulphuric acid, which in its turn yields sulphur, sulphide of arsenic, and sulphurous acid. When the distillation is completed, the glass tube of the condenser is washed, first with water, and then with a little weak ammonia. The precipitate is separated from the condensed liquid by filtration, and the filter is washed with dilute ammonia, which dissolves the arsenic trisulphide, and leaves the bulk of the sulphur. The filtrate, which will contain some sulphide of arsenic, produced by the action of the hydrochloric acid on the ammonical solution of sulphide of arsenic, is then treated with excess of sulphuretted hydrogen, and the sulphide of arsenic is collected on a weighed filter, washed with water, then with methylated spirit, afterwards with bisulphide of carbon, and, finally, with methylated spirit. The filter and contents are then dried at 100°, and the arsenic weighed as arsenic trisulphide, As_2S_3.

Antimony.—The distillation flask, after the removal of the arsenic, contains the antimony as trichloride, and the tin as stannic chloride, mixed with ferrous and ferric chloride and separated sulphur. The contents are passed through a filter and washed with water.

Of the different methods which have been proposed for the separation of antimony and tin, Tookey's, which is based on the precipitation of the antimony by means of metallic iron, could very easily be applied; but, unfortunately, it has been found to be impossible to get correct results by this method on account of the readiness with which the precipitated antimony oxidizes. Thiele (*Annalen*, **268**, 361) has shown that when electrolytic iron is used, the whole of the tin is thrown down along with the antimony, even in the cold; and I have observed that thin sheet iron frequently precipitates more or less tin when the solution is concentrated. Loveton (*Jour. Pharm.*, **17**, 361) has pointed out that sulphide of antimony is less soluble in hydrochloric acid than sulphide of tin,

and that, in solutions containing certain proportions of [illegible] chloric acid, the antimony and tin can be separated quantitatively by means of sulphuretted hydrogen. Lenssen recommends the precipitation of the antimony in a solution containing [illegible] ume of strong hydrochloric acid, and the collection of the [illegible] tate on cotton wool to prevent the destruction of the filter [illegible] hydrochloric acid, and he washes the sulphide of antimony [illegible] tate with a mixture of 1 part of hydrochloric acid [illegible] a saturated solution of sulphuretted hydrogen. Lenssen [illegible] only on alloys which he dissolved in hydrochloric [illegible] assistance of nitric acid or potassium chlorate [illegible] the sulphides of antimony and tin are subsequently [illegible] sulphide of sodium and electrolyzed, but he does not [illegible] results to show the accuracy of the process.

There can be no doubt, however, that in solutions [illegible] certain proportions of hydrochloric acid antimony can be [illegible] pletely separated from tin in this way. But when [illegible] potassium chlorate is used to effect solution it is not [illegible] know in what state of oxidation the antimony exists [illegible] could not be weighed as trisulphide without further treatment.

When ferric chloride is used as the oxidizing agent [illegible] tions are different. In this case the antimony exists [illegible] the form of trichloride and the tin as stannous [illegible] found however that in solutions containing [illegible] hydrochloric acid [illegible] precipitate the whole of the antimony [illegible] solution is diluted [illegible] time of strong hydrochloric acid [illegible] of sulphuretted hydrogen [illegible] of the antimony [illegible] process which [illegible]

The principal objection to Loveton's process, as carried out in this way, lies in the strict attention which must be paid to the proportion of acid and the necessity of washing with a mixture of hydrochloric acid and sulphuretted hydrogen water.

F. W. Clarke (*Chem. News*, **21**, 124) has shown that stannic sulphide, SnS_2, is soluble in a strong solution of boiling oxalic acid, but according to Wittstein and A. B. Clark, jun. (*Zeit. Anal. Chem.* **9**, 490), the oxalic acid process does not give results of any value when applied to mixtures of arsenic, antimony, and tin. According to F. P. Dewey (*Zeit. Anal. Chem.* **21**, 14), the failure of the process in their hands is due to the presence of free mineral acid, and he recommends the neutralization of the free acid, but finds it necessary to precipitate the antimony twice in a boiling oxalic acid solution to get it free from tin. From the results of my experiments, I am of opinion that Wittstein and Clarke's failure could not be due to a moderate quantity of free hydrochloric acid, and I have come to the conclusion that when the antimony exists in the form of trichloride, and the tin in the stannic state, as in the present case, a combination of F. W. Clarke's and Loveton's processes has advantages over either of them. The following are the details of this method:—The liquid from which the arsenic has been distilled is filtered to remove the sulphur, washed with water as far as necessary, then mixed with oxalic acid (about 20 parts of oxalic acid for 1 of mixed sulphides), dissolved in hot water, and sulphuretted hydrogen passed through the solution till it is cold. The solution should not be heated after the addition of the oxalic acid. Instead of passing the gas through the solution, excess of sulphuretted hydrogen water may be added; but in this case the antimony trisulphide precipitate should be filtered off shortly afterwards, as, on standing overnight, reduction takes place, and a little stannous sulphide is apt to be precipitated. In the presence of the oxalic and hydrochloric acid, only a portion of the ferric chloride is reduced, and the whole of the antimony is precipitated as antimony trisulphide, Sb_2S_3, absolutely free from tin, and mixed only with a little sulphur. The precipitate is collected on a weighed filter, and may be washed with any quantity of water without bringing down tin, and the filtrate gives no precipitate on the addition of a solution of sulphuretted hydrogen.

After being washed with water, the precipitate is washed with alcohol, then with carbon bisulphide, and finally again with alcohol the washings with alcohol and carbon bisulphide being kept separate. The filter and contents are dried, then digested in carbon bisulphide to ensure the complete removal of sulphur and weighed as antimony trisulphide, Sb_2S_3; small precipitates do not require to be digested in carbon bisulphide.

In the experiments which I have made to test the accuracy of the process, the precipitates have in every case been dried at [illegible] and then at 130°, but I am of opinion that when the antimony sulphide is thoroughly dried at 100° the loss of weight at 130° is so minute that in the case of small precipitates at any rate it may be disregarded.

Example

Sb₂S₃ first at [illegible]	Loss at [illegible]	[illegible]
[illegible] gm	[illegible]	[illegible]
[illegible] "	[illegible]	[illegible]
[illegible] "		
[illegible] "	[illegible]	[illegible]
Average		[illegible]

In these experiments, the sulphide of antimony was in each case removed from the filter, and dried first at 100° before it was heated to 130°.

I am aware it is generally believed that antimony trisulphide retains a little water which is not given off till it is converted into the black sulphide, which takes place between [illegible] and [illegible]. Lessen even recommends that the sulphide of antimony should be heated to this temperature before it is weighed, but he found it took as much as nine hours to get a constant weight in a current of air. There can be no doubt that antimony trisulphide suffers a loss of weight between [illegible] and [illegible], but I am of opinion that this is due not to water but to oxidation, for although the loss is small when the sulphide is heated for a short time it does not cease to lose weight, which it does for [illegible] hours daily for a week, if an open crucible with the filter and [illegible] gradually becomes brown, a color [illegible] to a mixture of oxide and sulphide.

The [illegible] experiments show the extent to which oxidation takes place under these circumstances.

	Weight of Sb_2S_3 dried at 130° taken.	Loss in about 30 hours at 200°–230°.	Sulphur in residue.	Sb_2S_3 corresponding to the sulphur.
(*a*.)	0.7782 gram	0.0657	0.0609	0.2157
(*b*.)	0.8187 "	0.0757	0.0525	0.1859

Sb_2S_3 per cent. in residue, (*a*.) 30.2 : (*b*.) 25.3.

These results indicate plainly that the antimony trisulphide is gradually converted into oxide when heated between 200° and 300°, and that it is of no use to heat the sulphide to this temperature. In my opinion, antimony trisulphide, dried at 130°, is anhydrous, and the most convenient form in which the metal can be weighed. I am also of opinion that it is less open to objection than any of the other forms in which antimony is frequently estimated. Bunsen (*Annalen*, **192**, 317) has pointed out that the temperature at which Sb_2O_3 is converted into Sb_2O_4 is so near the temperature at which the Sb_2O_4 is decomposed that he has given up this form as useless. It has also been recently shown by two independent observers, J. Thiele (*Annalen*, **268**, 361) and T. Wilm (*Zeit. Anal. Chem.*, **30**, 428), that the pentasulphide of antimony obtained by Bunsen's process contains a considerable quantity of free sulphur, and I have referred to the objections to weighing antimony as metal.

Tin.—The filtrate from the antimony precipitate, from which the alcohol and carbon bisulphide washings are excluded, contains the whole of the tin mixed with salts of iron and oxalic acid. To destroy the latter, the solution is heated, and solid permanganate of potash is added in small quantities at a time, till a precipitate of oxide of manganese is obtained which does not redissolve on boiling. Some ferrous salt is added to dissolve the oxide of manganese, and a stream of sulphuretted hydrogen is passed through the hot solution till it is quite cold. Under these circumstances, the tin, mixed with sulphur, is precipitated in a condition sufficiently dense to enable the precipitate to be collected and washed with water without showing any tendency to pass through the filter. When thoroughly washed, the filter and contents are dried, and the tin converted by ignition into stannic oxide, SnO_2, in which form it is weighed.

The following are the results which I obtained by this method :—

No. 1. Experiment with known quantites of antimony trichlor-

ide and stannic chloride in presence of oxalic acid and a [illegible] ble quantity of ferric chloride

	Taken	[illegible]
Antimony	[illegible] gm	[illegible]
Tin	[illegible]	[illegible]
Total	[illegible]	[illegible]

No. 2. Experiments on known quantities of [illegible] and tin, precipitated as sulphides, and afterwards treated [illegible] ric chloride and oxalic acid as described

Series With a small proportion of Arsenic

	Taken [illegible]	[illegible]	[illegible]	[illegible]
Arsenic	[illegible]	[illegible]	[illegible]	[illegible]
Antimony	[illegible]	[illegible]	[illegible]	[illegible]
Tin	[illegible]	[illegible]	[illegible]	[illegible]
Total	[illegible]	[illegible]	[illegible]	[illegible]

Series With a small proportion of Antimony

	[illegible]	[illegible]
Arsenic	[illegible]	[illegible]
Antimony	[illegible]	[illegible]
Tin	[illegible]	[illegible]
Total	[illegible]	[illegible]

Series With [illegible]

	[illegible]	[illegible]
Arsenic	[illegible]	[illegible]
Antimony	[illegible]	[illegible]
Tin	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

Series With [illegible] Metals

	[illegible]	[illegible]
Arsenic	[illegible]	[illegible]
Antimony	[illegible]	[illegible]
Tin	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

The only objection to the process which I have described is the necessity of digesting the sulphide of antimony with carbon bisulphide to remove the sulphur produced by the reduction of the ferric chloride. This difficulty can, however, by obviated by reducing the excess of ferric chloride before adding the oxalic acid. To effect this, I introduce a narrow strip of pure sheet iron into the solution after the removal of the sulphur and heat; reduction takes place in a few minutes. As soon as the yellow color of the ferric choride disappears, the undissolved iron is taken out; the antimony, which comes down to some extent before the ferric chloride is reduced, is removed by washing and rubbing, and to the solution containing the precipitate, the hydrochlric acid solution of ferric chloride is added drop by drop till the antimony dissolves, and the liquid acquires a permanent, yellowish tint indicating a slight excess of ferric chloride. The solution of oxalic acid (mixed in this case with about one-third of its bulk of hydrochloric acid) is then added, and the antimony precipitated with sulphuretted hydrogen, and washed with alcohol and carbon bisulphide, as already described.

Under these conditions, the quantity of free sulphur is so small that it is unnecessary to digest the precipitate with carbon bisulphide.

Example.

	Taken. Gm.	Found. Gm.
Antimony	0.1310	0.1302
Tin	0.1170	0.1232
Total	0.2480	0.2534

The hydrochloric acid is added to the oxalic acid solution to prevent the tin from being precipitated, as, in the absence of ferric chloride, tin is apt to come down along with the antimony sulphide when too little free acid is present.

These results indicate that the ferric chloride plays a very important part in the process; it is by its means that the antimony is always obtained in the form of trichloride. The ferric chloride also assists in preventing the precipitation of the tin, and renders it unneccessary to pay strict attention to the proportion of free acid.

For qualitative purposes, it is not necessary to employ a con-

denser in distilling off the arsenic; a bent tube dipping into water being sufficient, but it is advisable to use a safety tube to prevent the distillate passing back.

In the case of alloys or antimony ore, the metal or metals are dissolved in strong hydrochloric acid and ferric chloride, and the arsenic is distilled off at once. The sulphides of antimony and tin, after being separated from the other metals of the sulphuretted hydrogen group, are estimated as above.

A RAPID AND ACCURATE METHOD OF DETERMINING FAT IN MILK.*

By Henry Leffmann, M.D., and William Beam, M.D.

Among the processes for the rapid determination of fat in milk, those employing centrifugal machines have been most satisfactory. A procedure devised by us has proved, in the experience of others as well as ourselves, to be rapid, accurate, and economical. For the test, we employ a bottle holding about [illegible] cc., the neck of which is graduated so that a volume of [illegible] cc. is divided into [illegible] equal parts, [illegible] cc. of the milk being taken, each of these representing [illegible] per cent. by weight of butter fat. The test is made as follows:

[illegible] cc. of the milk are put into the bottle, [illegible] consisting of equal parts of fusel oil and strong hydrochloric acid are added, mixed, and strong sulphuric acid poured in, [illegible] with agitation, until the bottle is filled to the neck. The mixture comes hot, and the casein is completely dissolved, a [illegible] brown solution being formed. The neck is filled to near the [illegible] point with a hot mixture of sulphuric acid and water, [illegible] whirled in the centrifugal machine for [illegible] minutes. Milk very poor in fat may require more than this time. The volume of fat which [illegible] in the neck can be read off [illegible] or by the use of a pair of dividers. The points of the [illegible] rested in the upper and lower meniscus of the column of fat, being made by the movements from the dividers being [illegible] the [illegible] point [illegible] the [illegible] the [illegible] [illegible]

* [illegible]

We give herewith the results of comparative tests with the Adams' method, care being taken that the paper used was free from any extractable matter. The bottles employed in these tests were divided into 100 parts, and the figures here given were obtained by multiplying by the factor 0.86. (As noted above, we now use a bottle divided into 86 parts, and thus save calculations.):—

Whole Milk.

Sample.	Fat by Adams' Method.	Fat by Centrifugal Method
No. 1	3.534	3.53 3.56 3.56
No. 2	3.90	3.95 3.89 3.95
No. 3	3.03	2.97 2.97 2.93
Skimmed and Watered Milk.		
No. 4	0.56	0.51 0.51

Another determination was made of sample No. 4 by boiling down to one-half volume, and treating by the method, the results being calculated to the original volume. This gave 0.55 per cent. of fat.

Tests were made to determine the effect of longer rotation in the examination of milks poor in fat. Thus, by four minutes' whirling, the last sample gave, without previous concentration, 0.55 of fat.

Comparisons have also been made between the results of this method and the figures for fat as determined by calculation from the specific gravity and total solids (Hehner and Richmond's tables.)

Sample.	Fat by Calculation A. and R.	Fat by Centrifugal Method.
No. 5	3.60	3.61
No. 6	4.15	4.10

We find, as a result of many tests, that with bottles accurately graduated, and reasonable care in manipulation, especially sufficient rotation, results will be obtained within 0.1 per cent. of those of the standard methods.

715 WALNUT ST., PHILADELPHIA, PA.

ANALYSIS OF CHROMITE [illegible]

By E. Waterhouse [illegible]

Chromite, the mineral source of chromium compounds [illegible] the arts is essentially a chromate of iron and is represented [illegible] the formula FeO,Cr_2O_3. The theoretical composition [illegible] this basis, is:

FeO, 32 per cent
Cr_2O_3, 68 per cent

The mineral is frequently associated with magnesia [illegible] manganese, the full list of possible constituents [illegible] usually given for iron ores.

The chromium is usually the most important constituent [illegible] chrome oxide alone is determined. The refractory character of chromite is well known and many efforts have been made [illegible] to find a scheme of separation and estimation of the chromium which would be at the same time simple and accurate.

The following methods may be recalled. They [illegible] two distinct classes. First, those making use of [illegible]. Second, those in which fusion is used. Of the first class we [illegible] the following:

1. Boiling with nitric acid and potassium chlorate. [illegible] *Ber.* [illegible] Pearson, *Jour. Soc. Chem. Ind.* [illegible] Bullock, *J. Ind. Eng. Chem.* [illegible] Berlingin, *Jour. Soc. Chem. Ind.* [illegible] finds this method very satisfactory. Many others have found it tedious or inaccurate, and [illegible] our experience.

2. Heating with [illegible] water in a sealed tube at [illegible] C. for several days. [illegible] Smith, *Jour. Soc. Chem. Ind.* [illegible] It is obvious that the length of this operation [illegible]

3. Heating [illegible] C. with sulphuric acid [illegible] H_2SO_4 [illegible] Mitscherlich [illegible] **81.** [illegible] **83.** [illegible]

[illegible]

urged against these methods both from length of time required and danger of explosion. Of the second class, or fusion methods we find :

1. Acid potassium fluoride, Gibbs, *Fres. Zts.*, iii., 328, also Dubois, *Fres. Zts.*, iii., 401 ; these chemists use four to five times the weight of ore in flux and fuse from ten to fifteen minutes.

2. Alkaline or alkaline earth fluoride in conjunction with alkaline bi-sulphate, Sill, *Jour. Lond. Chem. Soc.*, xxxv., 292 ; Clarke *Am. Jour. Sci.*, 1868, 173 ; Hagen, *Untersuchungen*, i., 163. The use of fluorides requires special management to avoid the subsequent destruction of glassware and involves more manipulation, and skill than is required by some of the other methods.

3. Potassium bi-sulphate alone, Reinhardt, *Chem. Ztg.*, xiii., 430. This method is not efficient unless extraordinary precautions are taken in pulverizing the ore.

4. Potassium bi-sulphate followed by potassium chlorate and sodium carbonate, O'Neill, *Chem. News*, 1862, 199.

5. Potassium bi-sulphate followed by potassium nitrate and sodium carbonate, Oudesluys, *Chem. News*, 1862, 254; *Hunt, Amer. Jour. Sci.* [2], v., 418, adds a little alkaline nitrate towards the end of the operation.

6. Caustic alkali with or without the addition of lime, Pellet, *Berg. u Huttenman Ztg.*, xl., 224 ; Christomanos, *Ber.*, x., 10, substitutes magnesia for lime. Morse and Day, *Amer. Chem. Jour.*, iii., 163, advocate the use of an iron crucible.

7. Caustic or carbonated alkali in conjunction with an oxidizing agent. Potassium chlorate is recommended by Schwartz, *Annalen*, lxix., 212, and Blodgett-Britton, *Chem. News*, xxi., 226. Alkaline nitrate is recommended by Calvert, *Jour. Lond. Chem. Soc.*, v., 194 ; Peligot, *Comptes Rendus*, **67**, 871 ; Clouet, *Comptes Rendus*, **67**, 762. Barium dioxide is recommeded by Donath, *Ding. Polyt. Jour.*, cclxiii., 245 ; Kinnicut and Patterson, *Jour. Anal. Chem.* iii., 132.

8. Alkaline carbonates with borax, Dittmar, *Ding. Polyt. Jour.* ccxxi., 450 and Iron, January, 1876, p. 131. The flux is composed

of three parts of a mixture of potassium and sodium [illegible] with two parts of borax glass

9. Alkaline carbonate with some borax and alkaline [illegible] P. Hart. *Jour. Prakt. Chem.*, lxvii., 320.

The wet methods and those by fusion with fluoride have already been briefly discussed. Fusing alkaline bisulphate [illegible] experience does not readily decompose chromite unless it is in a state of subdivision not easily obtained. Elutriation is not a desirable method of obtaining the necessary state of comminution [illegible] the chromite possesses such a high specific gravity [illegible] that by elutriation a partial separation of that mineral from its associated minerals in any given sample will result, tending to produce [illegible] correct results.

Fusion with caustic alkalies requires the use of a silver [illegible] crucible. Such crucibles need to be thicker as compared [illegible] of platinum and consequently require the application [illegible] higher heat to keep the melt at the proper temperature during [illegible] Moreover, if oxidizing agents are used in these [illegible] deteriorate rapidly.

Of course where alkaline fluxes only are used the [illegible] is effected by the oxidation of the chromium [illegible] and its union with the alkali. The presence of an excess [illegible] with a plentiful excess of the oxygen of the air favors [illegible] and indeed is the method utilized in the manufacture [illegible] salts from the ore.

The following process based on such a fusion with [illegible] special treatment has been found to give satisfactory [illegible] proposed. The plan of procedure is:

1. Fuse [illegible] with twenty-six times its weight [illegible] mixture in a platinum [illegible]

2. Dissolve [illegible]

c. Take up with water containing a few drops of nitric acid, add hydrochloric acid and sulphurous acid, or a little ammonium sulphite, boiling out the excess of SO_2.

d. Neutralize with ammonia and boil, adding a little ammonium sulphide. Re-dissolve in hydrochloric acid, and reprecipitate as before to purify the precipitate. Ignite and weigh Cr_2O_3.

Comments—a. The flux is made by fusing together two parts of borax glass with three parts of (dry) sodium and potassium carbonates, mixed approximately in proportion of their molecular weights (106 to 138). After fusing the mixture is poured out upon a cold surface (a dry platinum dish floated on the surface of cold water) and then coarsely powdered for use. As it is somewhat hygroscopic, it should be kept in a tightly corked bottle. The borax makes the flux somewhat pasty, so that it holds the mineral partly in suspension, and thus favors the decomposition. A convenient form of dish for the fusion is one about 2 inches in diameter, and half an inch deep, with rounded bottom and provided with a small ear for grasping with the tongs. If a shallow dish of the kind is not available, the convexity of the cover of a large fusion crucible makes a very good substitute. The flux has practically no effect upon the platinum. Over three hours of fusion caused in one case a loss of 3.5 mgms. and ordinarily little or nothing.

A good way of managing the fusion is first to melt in the dish the requisite quantity of flux, and then allow it to cool; then weigh out the finely pulverized ore, and by means of a feather brush it on to the surface of the melt, spreading it as evenly as possible.

Then fuse with a good Bunsen burner, stirring occasionally with a platinum wire, until the decomposition is apparently complete. This is likely to require not over forty minutes, if the ore has been well pulverized, and the stirring has been sufficiently frequent. If either point has been neglected it may require longer. Remove the heat temporarily, and as the mass cools, stir with the platinum wire in such a way as to take a portion of the material from the bottom of the melt. As soon as this hardens sufficiently, withdraw and examine it for black grains of undecomposed ore. If any are seen, replace the test bead in the dish, cover, and apply the heat. The

material soon melts off from the wire, when the [illegible] moved, unless the heat is insufficient to keep the mass [illegible] out its use. When decomposition is apparently [illegible] the heat and allow the mass to cool.

b. The portion soluble in water, besides the excess [illegible] stituents of the flux, should contain all of the [illegible] chromate, together with some alkaline manganate [illegible] silicate. That insoluble in water should dissolve [illegible] hot dilute hydrochloric acid. If some black [illegible] posed ore remain, they must be filtered off and treated [illegible] more of the flux as in the first instance.

The evaporation of the water solution with [illegible] nitrate (*Zeitsch. Chem. N.*, [illegible]) causes the manganate [illegible] arate as insoluble MnO_2, the alumina being at the same time [illegible] cipitated as hydrate, which by the prolonged heating [illegible] form practically insoluble in nitric acid especially when [illegible] last addition of nitric acid and heating will render [illegible] insoluble, so that eventually nothing soluble remains except [illegible] line chromate and nitrate.

c. The object of this step is simply to reduce the [illegible] form of base. The presence of hydrochloric acid [illegible] in the next step as it affords ammonium chloride which [illegible] separation of chromium by heat.

d. It may be found that at first no precipitate appears [illegible] tralization with ammonia. [illegible] slight excess of ammonia. [illegible] precipitate [illegible] more with [illegible] washing [illegible] [illegible]

[illegible]

[illegible] method.

		Cr_2O_3 found. per cent.	Cr_2O_3 calc. per cent.
1.	Chromite and Iron Ore	4.18	4.38
2.	" "	2.92	2.80
3.	" "	3.87	3.96
4.	" "	2.75	2.64
5.	" "	2.57	2.72
6.	" "	2.98	2.88
7.	" "	4.44	4.32
8.	" "	4.027	4.07
9.	" "	8.44	8.64
10.	" "	3.52	3.51
11.	" "	2.77	2.907
12.	" "	10.37	10.60

These samples were made from a chromite mixed with iron and manganese ores. The chromite was found to contain 57.00 and 57.025 per cent. of chromic oxide as a result of determination by different analysts.

A RAPID METHOD OF DETERMINING THE COMPOSITION OF LUBRICATING OILS.*

By Harold Gripper, F. C. S.

The great majority of the oils now used for machine-lubricating are mixtures of hydrocarbon and saponifiable oils. The existing methods for the determination of these constituents are accurate and easily worked, but somewhat tedious, all consisting in saponification and subsequent separation by extraction of the hydrocarbons with ether. The usual process (described in Allen's *Commercial Organic Analysis*, vol. ii., p. 83) involves saponification, evaporation of the alcohol, dilution with water and cooling, separation in a separating funnel with ether, and finally evaporation of the ethereal layer and weighing of the residue. All this takes time, even if the separation in the separating funnel takes place rapidly, which is not always the case.

The following process I have found useful when a number of samples have to be examined at the same time, and when results approximately correct only are required, as is often the case in this laboratory. The results obtained are within two or three per cent. of the truth. The method is simply an extension of the

*Chemical News, vol. lxv., p. 27.

well-known Koettstorfer process. 2½ gms. of the sample are saponified in the usual way with 25 cc. of solution of alcoholic potash about $\frac{n}{2}$ (with oils containing more than 50 per cent of saponifiable oil the usual $\frac{n}{2}$ strength may be used). When saponification is complete the tritration is made in the ordinary way with $\frac{n}{2}$ HCl, using phenolphthalein as indicator, and a blank experiment having been made to estimate the strength of the alcoholic potash used, the percentage of KHO used by the sample is calculated.

The saponifiable oils chiefly used in the making of mixtures for lubricating purposes are:

	KHO absorbed per cent	Saponifiable matter per cent
Brown cotton seed	22.27	[illegible]
" rape	[illegible]	[illegible]
Neatsfoot	[illegible]	[illegible]
Lard	[illegible]	[illegible]
Tallow		
Castor	[illegible]	[illegible]

The potash absorptions therefore vary between [illegible] per cent and 22.27 per cent. It is necessary to take the mean of these figures (20.08 per cent) as the potash absorption of the unknown mixture of saponifiable matter in a lubricating oil. Thus $\frac{100}{20.08}$ = 4.98 parts of the oil are saponifiable by 1 part of KHO. Therefore if the percentage of KHO absorbed by the sample be multiplied by 4.98, the amount of saponifiable matter present will be obtained. Or the calculation may be simplified by multiplying the number of cc. of $\frac{n}{2}$ HCl corresponding to KHO absorbed by [illegible] × 4.98 = [illegible]. The proportion of saponifiable oils is thus obtained. The amount of hydrocarbon oil is ascertained by difference.

But it is necessary to know the specific gravity of the hydrocarbon oils. In order to estimate this the liquid in the [illegible] is immediately after titration poured again to the [illegible] and poured through a filter paper which has been saturated with boiling water. The alcoholic solution of soap and KCl [illegible] through in two or three minutes, the hydrocarbon oil remaining on the filter. This is washed once with boiling water and the specific gravity may then be taken by Hager's method. It is not

necessary to wash the oil more than once, since in making Hager's test the globule of oil dropped into the alcoholic liquid is immediately cleansed thereby from all impurities. The specific gravity of the hydrocarbon oils and of the original mixture being known, the specific gravity of the saponifiable oils may be calculated by difference.

By this method an analysis may be completed, including the calculation of results, within an hour of the commencement of the saponification, and in examining a series, it is of great advantage, a dozen samples being easily completed in a day. The only source of error is in the fact that the nature of the saponifiable oil, and therefore its exact saponification equivalent, is unknown.

	By Titration.		*By Separation and Weighing.*	
	Per cent.	Sp. gr.	Per cent.	Sp. gr.
I.	78.3 of hydrocarbon oil,	0.891		
	21.7 of saponifiable oil,	0.950		
	79.4 of hydrocarbon oil,	0.891	79.3 of hydrocarbon oil,	0.890
	20.6 of saponifiable oil,	0.955	20.7 of saponifiable oil,	0.957
	78.3 of hydrocarbon oil,	0.891		
	21.7 of saponifiable oil,	0.950		
II.	72.7 of hydrocarbon oil,	0.900	74.4 of hydrocarbon oil,	0.900
	27.3 of saponifiable oil,	0.973	25.6 of saponifiable oil,	0.979
III.	76.6 of hydrocarbon oil,	0.882	76.7 of hydrocarbon oil,	0.883
	23.4 of saponifiable oil,	0.956	23.3 of saponifiable oil,	0.953
IV.	65.4 of hydrocarbon oil,	0.887	64.1 of hydrocarbon oil,	0.886
	34.6 of saponifiable oil,	0.966	35.9 of saponifiable oil,	0.964
V.	79.9 of hydrocarbon oil,	0.885		
	20.1 of saponifiable oil,	0.963		
	79.6 of hydrocarbon oil,	0.885	79.8 of hydrocarbon oil,	0.886
	20.4 of saponifiable oil,	0.962	20.2 of saponifiable oil,	0.959
	79.9 of hydrocarbon oil,	0.885		
	20.1 of saponifiable oil,	0.963		
VI.	56.5 of hydrocarbon oil,	0.906	58.1 of hydrocarbon oil,	0.908
	43.5 of saponifiable oil,	0.966	41.9 of saponifiable oil,	0.965

The accompanying results were obtained by the process described, and by the usually accepted method of separation with ether and weighing the hydrocarbons. The results are in all cases in approximate and in some cases in close agreement.

A METHOD FOR THE ESTIMATION OF CHLORATES[1]

BY [illegible]

It has been shown in recent work in this [illegible] conditions properly controlled [illegible] expelling the iodine from hydriodic acid at the [illegible] time of the solution being itself reduced [illegible] to the equation

$$HAsO_3 + 2HI = HAsO_2 + H_2O + I_2$$

On cooling the liquid remaining after [illegible] titrating the arsenious acid present in the [illegible] oxidized volumetrically in the usual manner [illegible] accomplish this purpose being the excess [illegible] originally present as hydriodic acid and expelled [illegible] solution during the process [illegible]

In other words, [illegible] agents are present at the same time with the arsenious [illegible] be natural to suppose that the [illegible] the hydriodic [illegible] the [illegible] must be [illegible] [illegible]

rically and serving to measure the amount of iodide left undecomposed by the chlorate. Of course, the difference between the amount of iodide left undecomposed and that originally introduced should be the measure of the chlorate entering into the reaction. That a better form of iodometric method than those we have had heretofore for the estimation of chlorates is desirable is obvious when it is recognized that Bunsen's original process—consisting in heating the chlorate with hydrochloric acid and potassium iodide, distilling and estimating the iodine collected in the distillate—fails (owing to the formation of the comparatively non-volatile iodine chloride in the simultaneous action of the oxidizer upon hydrochloric and hydriodic acids) to show the entire amount of iodine corresponding to the chlorate; and that Finkener's substitute for this process—which prescribes the heating of the chlorate, under pressure in a closed bottle and in an atmosphere of carbon dioxide, with a mixture of hydrochloric acid and potassium iodide previously prepared by treatment with sulphurous acid, boiling and subsequent cooling in an atmosphere of carbon dioxide—though excellent when properly carried out, demands careful preparation of materials and skillful handling in the execution.

We have studied the applicability of the process outlined above, and record our experience in the following account.

A solution of potassium iodide, approximately decinormal, was standardized according to the method to which reference has been made, and which may be summarized in brief, as follows: Portions of this solution were measured from a burette into Erlenmeyer beakers capable of holding 300 cc., 2 gms., approximately, of pure dihydrogen potassium arseniate were added in solution, 20 cc. of a mixture of sulphuric acid and water in equal volumes were introduced with enough water beside to increase the entire volume to a little more than 100 cc. A platinum spiral was introduced to secure quiet boiling, a trap made of a straight two-bulbed drying tube cut short was hung with the larger end in the neck of the flask, and the liquid was boiled until the level had reached a mark upon the flask indicating a volume of 35 cc., experience having shown that this degree of concentration is sufficient, and that it is best not to exceed it. The liquid remaining was cooled and

nearly neutralized by sodium hydrate, acid potassium [illegible] was added to alkalinity, 20 cc. of a saturated solution [illegible] were added in excess, and the arsenious oxide in solution was titrated by standardized decinormal iodine in presence of starch. The iodine added in the reoxidation of the arsenious oxide was taken as the exact equivalent of the iodine expelled [illegible]. Several closely agreeing determinations made in this manner served to fix the standard of the solution.

The action of chloric acid under similar conditions was tested by following out exactly the process employed in standardizing the iodide, with the exception that weighed amounts of potassium chlorate, purified by recrystallization, were also introduced, and that the precaution was taken to have the potassium iodide present in every case to an amount at least eight and a half times as great as that of the potassium chlorate [illegible] than the equivalent weight of the iodide required [illegible]. The experiments involved amounts of the chlorate [illegible] 0.2 gm. to [illegible] gm., and quantities of the iodide [illegible] eight and a half to fifty times those of the chlorate. The results with all essential details are contained in the following table.

[illegible]

The mean error of these determinations is a little less than 0.0002 gm. +, between extremes of 0.0005 gm. + or 0.0005 gm. —, and the results are evidently excellent for an iodometric process in which titration is effected by decinormal solutions.. An excess of iodide over an amount a little in excess of the equivalent proportion is without effect. The process is rapid and easy.

The paper upon the determination of iodine, to which reference has been made and upon which this process is based, prescribes corrections for the volatility of arsenious chloride and the slight deoxidation of arsenic acid when chlorides and bromides are also present in considerable amount. In this process, however, the amount of hydrochloric acid evolved from the maximum weight of chlorate treated—0.2 gm. of the potassium salt—calls for a correction so small as to be insignificant.

NEW BOOKS.

Landis' Volumetric Tables.*—The following extracts explain clearly the purpose of the tables.

"In the following tables, columns Fe and Fe% are used with Bichromate and Permanganate, the other columns with the latter only. Column Fe gives the Iron, and may be used for CaO by titrating the oxalate, calculating as if for Fe, and dividing by 2 = CaO.

Column Fe% is used when 1 gm. of ore is taken, dissolved, diluted to 250 cc., and 50 cc. taken for titration, and gives the percentage directly. Column W. gives the Mn by Williams' method, V. the Mn by Volhard's method, and E. the Phosphorus by Emmerton's method.

STANDARDIZING.

Weigh off 1.4 gm. ferrous ammonium sulphate, place in beaker, add water and sulphuric acid, and titrate. The number of cc. used shows the proper table for that strength of solution.

EXAMPLES.

The following examples, taken from actual practice, will ex-

*Volumetric Tables for Pig Iron, Steel and Ore Analysis. By E. K. Landis, Pottstown, Pa. Leather cover, pocket-book size. Published by the author. Price, 50 cents

plain the use of the tables. The permanganate solution took 35.8 cc. to titrate 1.4 gms. ammonium ferrous sulphate [illegible] 2 gms. Fe. 1 gm. of ore was dissolved, diluted to 250 cc. and [illegible] titrated taking 10.7 cc. permanganate. By table 35.8

TABLE

35.8 cc. [illegible] 2 Fe

	Fe	Fe	W	[illegible]	[illegible]
1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible] Fe [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] Fe

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WIBORGH'S COLORMETRIC SULFUR DETERMINATION.

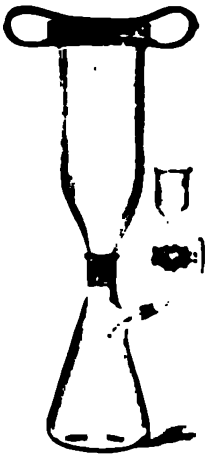
BY H. C. BABBITT, B.S.

The sulfur method of Dr. Wiborgh is used exclusively in nearly all the large steel works and blast furnaces in Sweden, and is particularly valuable where a large number of determinations are made, or only a small amount of drillings is available for analysis. The principle involved is the evolution of hydrogen sulfid from the sample by dilute sulfuric acid in a special apparatus, its absorption in a cloth saturated with cadmium acetate, and the comparison of the yellow color of cadmium sulphid with a set of standard colors. With proper precautions, results agreeing to within .01 per cent. are easily obtained in twenty minutes.

The apparatus consists of a generating flask of about 250 cc. capacity, with a side tube for admission of acid; a cylinder, with flanged top, ground into the neck of the flask, the upper face of the cylinder being ground flat; two rubber washers of 55 mm. internal diameter, a heavy wooden ring somewhat larger, and a pair of strong clamps.

The *modus operandi* is as follows: The weighed sample of drillings, from .8 to .1 gm., is placed in a small test tube, to which is attached a fine platinum wire about .3 mm. diameter, and transferred to the generating flask, which is partially filled with water, and placed over a suitable burner. The cylinder is then adjusted, and the water brought to boiling. A rubber washer is then placed on the top of the cylinder, followed by the prepared cloth, the second washer, and the wooden ring, the whole being firmly clamped together. Be sure the top of the cylinder is in a hori-

zontal position. As soon as the cloth is moistened and the air driven from the apparatus, about 12 cc. dilute sulphuric acid or 40 is admitted through the side tube, and a gentle heat applied till the sample is in solution. The cloth is then [illegible] dried on a blotting or filter paper, and compared with the [illegible] and colors. The proper construction of the apparatus is essential to the [illegible] of the determination. The ground surface of the cylinder must be perpendicular to the axis of axis, and the axes of the cylinder and [illegible] ting flask must coincide. The [illegible] inder must be so large that [illegible] will not spurt on the cloth spotting [illegible] small that the evolved gases will [illegible] distributed through the cylinder. The same diameter of cloth must always [illegible] the action of the evolved gases. A [illegible] about 7 inches high and [illegible] diameter, fills these conditions [illegible] a rubber washer 55 mm diameter [illegible] ent size for the apparatus that diameter of cloth [illegible] exposed.



Preparation of Cloth. The cloth must be [illegible] that the evolved gases will not pass through the [illegible] and must be so impregnated with [illegible] the maximum amount of sulphur. The [illegible] solid [illegible] formed on the surface otherwise [illegible] solid. Filter paper was found to be easily [illegible] most [illegible] waste [illegible] of mercerized cotton [illegible] Sachsen [illegible] Page [illegible] adopted. [illegible] were tried [illegible] [illegible] The [illegible]

[illegible] The [illegible]

cent. sulfur in 0.4 gms. of sample. Taking this as a maximum, Dr. Wiborgh prepares a color scale, neatly arranged on folding cards, as follows:

Color No.	7 = .10	per cent.	in 4 gms.	of sample.		
" "	6 = .07	"	"	"	"	
" "	5 = .05	"	"	"	"	
" "	4 = .03	"	"	"	"	
" "	3 = .02	"	"	"	"	
" "	2 = .01	"	"	"	"	
" "	1 = .005	"	"	"	"	

By taking the proper amount of a sample of known sulfur content, the preparation of these standards is obvious. To facilitate calculation, on the bottom of each card is printed the calculation for varying weights of sample taken. Thus if W = weight of sample taken, and s = corresponding sulfur for that color,

Color No. 6.

W.		S.
.8 gm.	=	.035
.4 "	=	.070
.2 "	=	.140
.1 "	=	.280
.08 "	=	.35
.04 "	=	.70
.02 "	=	1.40

The colors most easily read are 3, 4 and 5, so when the approximate sulfur is known, *i.e.*, high or low, an amount can be taken which will come within these limits.

The standard colors and prepared cloths can be purchased, as well as the glass apparatus, which is made in accordance with Dr. Wiborgh's design.

I wish to acknowledge my indebtedness to Mr. C. F. Treadway for his translation of Dr. Wiborgh's article, and to Messrs. Bullock & Crenshaw for the promptness with which they imported for me the necessary apparatus.

WELLMAN IRON & STEEL CO.,
THURLOW, PA.

ON THE MANUFACTURE OF THE CINCHONA ALKALOIDS

By Walter D. [illegible]

PART II

In part I of this paper[1] the author endeavored [illegible] an economical method of procedure to extract the alkaloids [illegible] the cinchona bark. In this part, the methods of separating the alkaloids from each other on a commercial scale are given.

The separations of the several alkaloids are based [illegible] properties, as follows:

1. Separation of quinin from cinchonin (quinidin [illegible] cinchonidin).
   a. Slight solubility of quinin sulphate in water.
   b. Slight solubility of the normal tartrate of quinin.

2. Separation of cinchonidin from quinidin and [illegible]
   a. Slight solubility normal tartrate cinchonidin [illegible] water and easy solubility tartrates of cinchonin and quinidin.

3. Separation of quinidin from cinchonin.
   a. Slight solubility of the acid tartrate of quinidin [illegible] water.

4. Separation of cinchonin and quinidin [illegible] in [illegible] sulphuric acid [illegible] the basic properties [illegible]

5. Separation of quinin, cinchonidin and quinidin [illegible] the cinchonin precipitate by treatment with [illegible]

6. Separation of dissolved and suspended alkaloids [illegible] solubilities.

SEPARATION

The acid solution of the alkaloids is [illegible] mixed [illegible] with [illegible] and [illegible] a saturated [illegible] solution of the alkaloids [illegible] kept [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] After [illegible]

The kettles or boilers used for heating and neutralizing the liquors are made like any ordinary water tank, lined with lead, and provided with agitators. They may be heated by steam direct or by using a coil. If steam is blown directly into the solution, the bottom of the kettle where the steam strikes must be protected by a sheet of copper, and even then the lining of the kettle will soon be riddled with minute holes. When the steam is introduced by a coil, the lining of the kettle lasts longer, but the bottom of the kettle is much more difficult to clean, as the steam coil covers the bottom. Although to the author's mind the practice of blowing steam direct into the alkaloidal solution is very pernicious, yet it is very general in this country. It is pernicious not only from its effect on the kettle, but also because of its undoubted decomposing action upon the alkaloids. In England and on the Continent coils are almost universally used for heating purposes. The liquor having settled, is now ready to run into the crystallizing boxes. The cock inside of the kettle is placed about 4 or 6 inches from the inside bottom, which admits of the bone-black settling. However, the liquor must be strained before crystallizing. Sand strainers were tried, but were found too bulky, hard to clean, and got easily choked while the liquor was running through. Finally a filter bag was adopted which was like a coat sleeve turned inside out and cut off square at the shoulder, or resembled two hollow cylinders, one inside the other, and fastened together at the bottom, leaving the center open. The filter bag is applied to the cock by inserting the cock between the inside and the outside cylinders of cloth, thus producing a filtering surface on the inside as well as the outside.

To crystallize, the neutralized solution of the alkaloids is run into a lead-lined box. This box may be one of many shapes. The smaller the box, the quicker the crystallization, but they are more expensive to produce, and require a large floor space. A larger box does not cost so much more, and the crystallization can be forced by agitation. These remarks do not apply to the final crystallization of the sulfate quinin.

A good shape for a crystallizing box is about 6 feet square and 2 feet 6 inches deep, lined with 8-pound lead, and provided with an agitator. Batches run from the kettles at a temperature of

77° to 80° C., are about 65° to 70° C. when they reach the crystallizing box, and by running the agitators during the night, the crystals can be filtered the first thing the next morning.

For filtering, an A. L. C. Dehne through extraction filter press is all that could be desired. For pumping the crystal mush into the press, use a Guild and Garrison "D" filter press pump. This combination of press and pump produces a pressed cake having from 40 to 64 per cent. of moisture in it. The average percentage of moisture in the pressed cake is about 50 per cent. The crystals from the first crystallization of the alkaloids contain an average of 12.6 per cent. insoluble alkaloids. On recrystallizing, the crystals are found to contain about 5 per cent. insoluble sulfates. This recrystallization is continued until the quinin sulphate crystals are practically free from cinchonidin. The boxes used for the last crystallization need to be shallow and small, and arranged so that the crystals can be rapidly drained. A good form is given in Fig. 1. It is 5½ feet long, 3 feet wide, and 6 inches deep, lined with 4 or 6-pound lead. A lead nozzle is burned to the lining at *c*, to which may be fastened a hose for running the liquors from the crystals back to the tanks. The box is hinged at *a* and *b*, so that it can be raised at the rear gradually, to allow the crystals to drain. When drained, they are cut into blocks by a knife, placed on frames made of a wooden frame covered with muslin and heavy unsized paper. For the purpose of hastening the drying, the temperature is kept quite high, about 70° to 80° C., just sufficient to slowly dry the crystals without their losing their water of crystallization. The drying room must be provided with an exhaust fan. The liquor run from the final crystallization is used for dissolving crude crystals again.

The liquors which come from the filtering presses are run into tanks on the floor below, then pumped up into precipitating kettles, where the alkaloids are precipitated with carbonate of soda (soda ash), the soda liquor run into tanks, the precipitate strained and washed, then dissolved in dilute acid, neutralized and crystallized. This time the crystals contain about 34 per cent. insoluble alkaloids. The liquor filtered from these crystals is precipitated as before, the precipitate washed, and then dissolved, neutralized and crystallized, and this time the crystals test about 49 per cent. insoluble alkaloids.

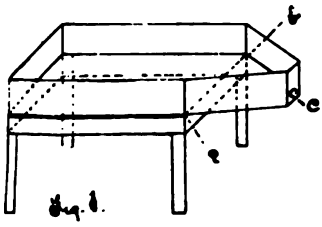


Fig. 1.

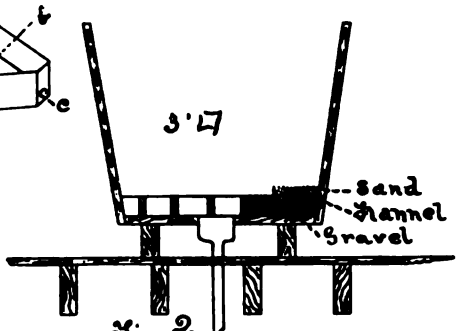
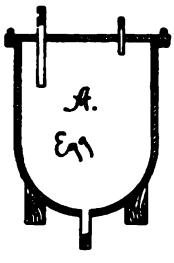


Fig. 2.



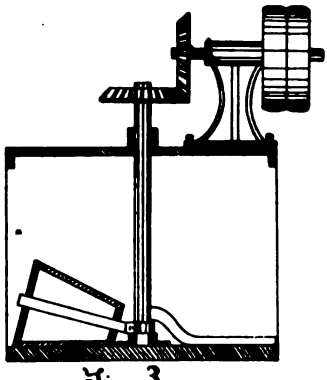


Fig. 3.

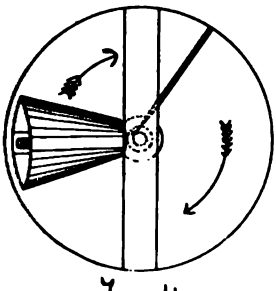


Fig. 4

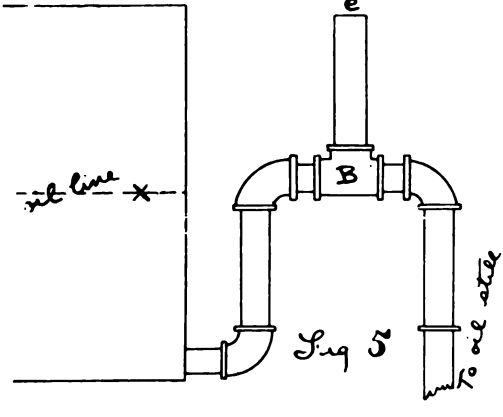


Fig 5

By recrystallization, these batches of crystals are finally reduced in their percentage of insoluble alkaloids, until finally they are ready for final crystallization.

At this point in the separation of the alkaloids, it becomes necessary to adopt other methods, as the alkaloids will no longer crystallize as sulfates. The normal tartrates of quinin and cinchonidin are very much less soluble in water than the normal tartrates of cinchonin and quinidin. The liquor from the crystals, which contain about 49 per cent. insoluble alkaloids, is run into a tank, precipitated with concentrated solution of sodium hydrate, the soda liquor run off, water added, and enough tartaric acid to decompose the precipitate; the solution must be hot during the operation. The solution is nearly neutral when run into the crystallizing boxes. The addition of bone-black is not required in any batches, except those crystallizing as sulfates. As the amounts of this liquid are never large, even in a factory producing 7000 ounces per week, a crystallizing box 3 or 4 feet wide by 7 or 8 feet long and a foot to a foot and a half deep is a good size.

It may be necessary to allow a day or more for the normal tartrates of quinin and cinchonidin to crystallize, as the amorphous alkaloid exerts a retarding influence on the crystallization.

A filter press can be used to filter the normal tartrates, but they are so thick the plates of the press are very rapidly destroyed on account of the extra pressure required.

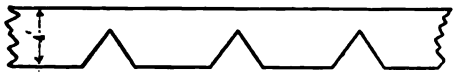
The normal tartrates of quinin and cinchonidin are decomposed with sodium carbonate, the sodium tartrates being run off in a tank, to have the tartaric acid reclaimed. All the sodium tartrate liquors should be run into this tank and then worked into tartaric acid when the amount is sufficient.

The liquor from the normal tartrates contains the quinidin and cinchonin, together with the amorphous alkaloid. The acid tartrates of these are now produced by adding 18 pounds tartaric acid for every 16 pounds used in producing the normal tartrates. Heat the liquor while adding the tartaric acid, and raise to near the boiling point before running into the crystallizing boxes. After an interval of twelve to twenty-four hours, the acid tartrates of quinidin and cinchonin separate, resembling a thick mush. The crystals cannot be filtered in a filter press, but can

be filtered in a centrifugal press, and afterwards washed without removing from the press.

The liquor from the acid tartrates is precipitated with sodium carbonate, the precipitate transferred to a filter, such as is represented in Fig. 2, and then washed with 66° B. sulfuric acid by the aid of a vacuum pump, operated through the egg *A*.

The filter box (see Fig. 2) is lined with good heavy lead—14 to 16 pounds to the square foot. An opening is left in the bottom for connection with the exhaust chamber. On the bottom is put 3 to 4 inches coarse gravel, about the size of small marbles, divided in sections by strips of wood ⅞ inch thick, notched on the bottom thus,



to allow for the passage of the liquor on the bottom of the filter. The strips are placed from 4 to 5 inches apart, on edge with the notches down. The gravel should be flush with the top of the wooden strips. On the gravel layer place a piece of good flannel, that is, free from cotton, or else once using will render it useless. Let the edges of the flannel piece run up on the sides of the filter 1½ to 2 inches. Now fill on top of the flannel clean sand to the top of the turned-up edge. The sand must be packed down tight and the filter must be washed quite often. In washing, remove sand and gravel; wash in pail with dilute sulfuric acid. The filter is best operated thus:

The precipitate to be treated is put in the filter, and then pressed down all around the edges and the pump started. As soon as the pump begins to draw, commence pouring the 66° B. oil vitriol on the precipitate, taking care to distribute the acid evenly. The acid removes the basic chinoidin by reason of its being more easily soluble than the cinchonin and cinchonidin and quinidin. The pump is run until all the acid is removed from the precipitate, which is now a light gray color. The precipitate is now ready for extraction by mixed oil, to separate cinchonin from cinchonidin and quinidin. This is done by placing the precipitate in a digester (see Fig. 3), by means of which the precipitate is kneaded with mixed oil several times, each time allowing to settle, and

the clear oil drawn off and put in tank to be washed with dilute sulfuric acid.

The roller of the digester is so arranged that it accommodates itself to the uneven character of the bottom of the tank caused by the precipitate. The digester is set with the bottom inclined toward the draw-off spout, to facilitate removing the charge. When the precipitate is thoroughly worked, it is removed and put into a tank and agitated with a much larger quantity of oil. After several hours the cinchonin is allowed to settle, and the oil layer containing the last traces of quinin and cinchonidin is separated and washed with dilute sulfuric acid.

The batches of precipitated normal tartrates and acid tartrates are combined with sulfate crystal batches, with which they correspond in test, and so on throughout the manufacture it must be the endeavor of the manager to condense liquors, precipitates and crystals as much as possible.

The acid sulfate cinchonin drawn from the egg of the filter is precipitated with caustic soda, the soda liquor removed and the resinous precipitate evaporated to dryness.

RECOVERY OF WASTE

For a long time no endeavor was made to extract the alkaloids remaining in the bone black used for decolorizing the liquors, but it was found that when treated in the same manner as the [illegible] the alkaloids could be extracted. This is now being [illegible] with success.

The workmen with their careless manipulation in running off a soda liquor after precipitation of the alkaloids when some of the precipitates are still floating will [illegible] a large amount of [illegible] time. To avoid this waste the soda liquors are all run into tanks where they are neutralized and precipitated with caustic soda, agitated with [illegible] the mixed oil washed with acid and the acid solution of the alkaloids returned to the gum tank extract and thus [illegible].

In Fig. [illegible] is given a simple arrangement for carrying the separation [illegible] soda liquors. The tank is filled with [illegible] mixed [illegible] the soda liquors are run into the [illegible] agitated. When settled the soda liquor is run off by

the siphon *B*. When the liquid reaches the level of the top of the siphon, air enters at *C*, and the siphon ceases to work, and the oil remains in the tank.

By this simple arrangement the separation of oil and water is complete, and stops when ended, even though the workmen may not be present.

The solution of alkaloids thus obtained is washed with dilute sulfuric acid, and the acid solution of the alkaloids returned to the original liquor for crystallizing.

All soda liquors are run into a still, and the dissolved oil is distilled off. This still must be run day and night, and sometimes two or more are necessary to keep the soda liquors out of the way. They are of simple construction, just a large boiler iron tank with a coil in it, and an outlet attached to a cooling room. The distillation is worth the expenditure of money and space, as it reclaims about 7 per cent. of the oil, and needs no attention in working.

All sinks in the factory must have their outlets run into a precipitating tank, and the alkaloids, from washing mops, ladles, shovels, etc., etc., reclaimed. This is a most important point, and should not be neglected.

NOTES ON THE ANALYSIS OF THE NITRO-EXPLOSIVES.

By P. Gerald Sanford, F.I.C.,F.C.S.

Now that the various forms of nitro-compounds are gradually replacing the older forms of explosive agents, both for blasting purposes and also as a propulsive agent, perhaps some notes upon the methods for their analysis, and examination, that I have used and found to work satisfactorily, may be of service to other chemists, who may be engaged upon similar work. The class of compounds that have come into the most extended use for the purposes of mining, blasting, etc., are the nitro-glycerin compounds, more especially the gelatine compounds, composed of nitro-cellulose and nitro-glycerin, and generally containing some admixture of nitrates and wood pulp, or similar materials.

KIESELGUHR DYNAMITE.

This material generally consists of 75 per cent. nitro-glycerin

and 25 per cent. of the infusorial earth Kieselguhr. The analysis is very simple, and may be conducted as follows: Weigh out about 10 gms. of the substance, and place over calcium chlorid, in a desiccator, for some six to eight days, and then reweigh; the loss in weight gives the moisture; this will generally be very small, probably never more than 1 per cent. The dry substance may now be wrapped in filter paper, the whole weighed, and the nitro-glycerin extracted in the Soxhlet apparatus with ether. The ether should be distilled over at least twenty-four times. I have found, however, that results may be obtained much quicker, and quite as accurate, by leaving the dynamite in contact with ether in a small Erlenmeyer flask for some hours,—leaving it over night is better,—and then decanting, and again allowing the substance to remain in contact with the ether for a few hours, and finally filtering through a weighed filter, drying at 100° C., and weighing. This gives the weight of Kieselguhr. The nitro-glycerin must be obtained by difference, as it is quite useless to evaporate down the ethereal solution to obtain it, as it is itself volatile to a very considerable extent at the temperature of evaporation of the ether, and the result, therefore, will always be much too low. An actual analysis of Kieselguhr dynamite gave: Moisture, 0.92 per cent; Kieselguhr, 26.15 per cent.; and nitro-glycerin, 72.93 per cent., this last being obtained by difference.

GELATINE COMPOUNDS.

The simplest of these compounds is, of course, blasting gelatin, as it consists of nothing but nitro-cotton and nitro-glycerin, the cotton being dissolved in the glycerin to form a clear jelly, the usual proportions being about 92 per cent. of nitro-glycerin to 8 per cent. of nitro-cotton, but the cotton is found as high as ten per cent. in some gelatines. Gelatine dynamite and gelignite are blasting gelatines with varying proportions of wood pulp and saltpeter (KNO_3), mixed with a thin blasting gelatin. The method of analysis is as follows: Weigh out about 10 gms. of the substance, previously cut up in small pieces, and place over calcium chlorid in a desiccator for some days. Reweigh; the loss equals moisture. This is generally very small. The dried sample is then transferred to a small thistle-headed funnel which has been

cut off from its stem, and the opening plugged with a little glass wool, and round the top rim of which a piece of fine platinum wire has been fastened, in order that it may afterwards be easily removed from the Soxhlet tube. The weight of this funnel and the glass wool must be accurately known. It is then transferred to the Soxhlet tube and exhausted with ether, which dissolves out the nitro-glycerin. The weighed residue must afterwards be treated with ether-alcohol to dissolve out the nitro-cotton.

But the more expeditious method is, perhaps, to transfer the dried gelatin to a conical Erlenmeyer flask of about 500 cc. capacity, and add 250 cc. of a mixture of ether-alcohol (2 ether to 1 alcohol), and allow to stand over night. (Sometimes a further addition of ether alcohol is necessary, but not often.) The undissolved portion, which consists of the wood pulp, and potassium nitrate, and other salts, is then filtered off, dried, and weighed.

Solution.—The ether-alcohol solution contains the nitro-cotton and the nitro-glycerin, in solution. To this solution add excess of chloroform, when the nitro-cellulose will be precipitated in a gelatinous form. This should be filtered off through a linen filter, and allowed to drain. It is useless to attempt to use a filter pump, as it generally causes it to set solid. The precipitated cotton should then be redissolved in ether alcohol, and again precipitated with excess of chloroform. This precaution is absolutely necessary, as otherwise the results will be much too high, owing to the gelatinous precipitate retaining very considerable quantities of nitro-glycerin. The precipitate is then allowed to drain as completely as possible, and finally dried in the air-bath at 40° C. until it is easily detached from the linen filter by the aid of a spatula, and then transferred to a weighed watch-glass, replaced in the oven, and dried at 40 degrees until constant in weight. The weight found, calculated upon the 10 gms. taken, gives the percentage of nitro-cellulose.

The *residue* left after treating the gelatin with ether-alcohol is, in the case of blasting gelatin, very small, and will probably consist of carbonate of soda. It should be dried at 40° C., and weighed, but in the case of either gelignite, or gelatine dynamite, this residue should be transferred to a beaker and boiled with distilled water, and the water decanted three or four times, and the

residue finally transferred to a tared filter and washed [illegible] time with hot water. The residue left upon the filter is wood pulp. This is carefully dried at 40° C., until constant and weighed. The solution and washings from the wood are evaporated down in a platinum dish and dried at [illegible] C. in the oven and weighed. It will consist of the potassium nitrate and any other mineral salts, such as carbonate of soda which [illegible] always be tested for by adding a few drops of nitric acid and a little water to the residue, and again evaporating to dryness and re-weighing. From the difference in weight the soda can be calculated, sodium nitrate having been formed.

The nitro glycerin is best found by difference, but [illegible] the solutions from the precipitation of the nitrocellulose may be evaporated down upon the water bath at 90 to [illegible] C. [illegible] dried over $CaCl_2$ until no smell of ether can be detected, [illegible] nitro glycerin weighed. It will, however, always be [illegible] low. An actual analysis of a sample of gelatin dynamite gave the following result:

Nitrocellulose	[illegible]
Nitroglycerin	[illegible]
Wood pulp	[illegible]
KNO_3	[illegible]
Water	[illegible]
	[illegible]

This sample was probably intended to contain [illegible] absorbing material to [illegible] per cent of explosive substance.

[illegible] C. [illegible] and other [illegible] lost [illegible] the Hexanitrocellulose and lower nitro [illegible] The first thing upon [illegible] wet gun cotton [illegible] a sample from the press [illegible] requires [illegible] the percentage of water [illegible] [illegible] water. [illegible] wet gun cotton.

[illegible] of this test is [illegible]

the case of gun-cotton, the percentage of soluble (penta and lower nitrates) cotton that it contains, or in the case of soluble cotton, the quantity of gun-cotton. The method of procedure is as follows: 5 gms. of the sample, which has been previously dried at 100° C. and afterwards exposed to the air for two hours, is transferred to a conical flask and 250 cc. of ether-alcohol added. The flask is then corked and allowed to digest, with repeated shaking, for two or three hours. The whole is then transferred to a linen filter, and when the solution has passed through, the filter is washed with a little ether and pressed in a screw-press between folds of filter paper. The sample is then returned to the flask, and the previous treatment repeated, but it will be sufficient for it to digest for one hour the second time. The filter is then opened up, and the ether allowed to evaporate. The gun-cotton is then removed from the filter and transferred to a watch-glass, and dried in the water oven at 100° C. When it is dry, it is exposed to the air for two hours and weighed. It equals the amount of gun-cotton and unconverted cotton. In the 5 gms., the non-nitrated cellulose must be determined in a separate 5 gms. and deducted.

ESTIMATION OF THE NON-NITRATED COTTON.

However well the cotton has been nitrated, it is almost certain to contain a small quantity of non-nitrated or unconverted cotton. This can be determined thus: 5 gms. of the sample are boiled with a saturated solution of sodium sulfid, and then allowed to stand for forty-eight hours, and afterwards filtered or decanted, and again boiled with fresh solution of sulfid, and again filtered, dried and weighed. The residue is the cellulose that was not nitrated. It should be ignited, and the weight of the ash deducted from the previous weight.

ALKALINITY.

5 gms. of the air-dried and very finely-divided sample are taken from the centre of the slabs or discs and digested with about 20 cc. of $\frac{n}{4}$ hydrochloric acid, and diluted with water to about 250 cc., and shaken for about fifteen minutes. The liquid is then decanted and washed with water until the washings no longer give an acid

reaction. The solution, together with the washings, are then [illegible] trated with $\frac{N}{10}$ sodium carbonate, using litmus as indicator [illegible]

NITROGEN

The estimation of the percentage of nitrogen in a sample of gun cotton or collodion cotton, is perhaps of more [illegible] and affords a better idea of its purity and composition than [illegible] the foregoing methods of examination, and taken in conjunction with the solubility test, it will generally give the analyst a very fair idea of the composition of his sample. If we regard gun cotton as the Hexa nitro cellulose $C_6H_4O_4(ONO_2)_6$, the theoretical amount of nitrogen required for the formula is 14.14 per cent. [illegible] the same way for collodion cotton, which consists of the lower nitrates, that is the penta and tetra nitro bodies, the theoretical nitrogen is 11.11 per cent. and 9.76 per cent. respectively. [illegible] a sample of gun cotton the nitrogen falls much lower than [illegible] per cent. it probably contains considerable quantities of the lower nitrates, and perhaps some non nitrated cellulose, as well as $C_6H_{10}O_5$, which of course would also lower the percentage of nitrogen. The most expeditious method of determining the nitrogen in these nitro bodies is by the use of Lunge's nitrometer, and the best way of working the process is as follows. Weigh out with the greatest care [illegible] gm. of the previously dried cotton in a [illegible] weighing bottle or [illegible] and carefully [illegible] trated sulphuric acid from a pipette. Allow to stand [illegible] the cotton is dissolved. The nitrometer should be [illegible] the top and should be filled with Greiner & Friedrichs' way tap. When the [illegible] solution from the pipette [illegible] the nitrometer [illegible] the top [illegible] the [illegible] paper. [illegible] the [illegible] Now [illegible] the [illegible] Now [illegible] the [illegible]

a little, just enough to cause the solution to flow into the bulb of the measuring tube, when the tap is slightly opened. When the solution has run in almost to the end, turn off the tap, wash down the sides of the bottle, and add to the cup of the nitrometer; allow it to flow in as before, and then wash down the sides of the cup with 10 cc. of sulfuric acid, adding little by little, and allowing each portion added to flow into the bulb of the nitrometer before adding the next portion. Great care is necessary to prevent air-bubbles obtaining admission, and if the pressure tube is lowered too far, the acid will run in with a rush and carry air along with it. The solution being all in the measuring tube, the pressure tube is again slightly raised, and the tube containing the nitro-cotton-solution shaken for ten minutes with considerable violence. It is then replaced in the clamp and the pressure relieved by lowering the pressure tube, and the whole apparatus allowed to stand for twenty minutes, in order to allow the gas evolved to assume the temperature of the room. A thermometer should be hung up close to the bulb of the measuring tube. At the end of the twenty minutes, the levels of the mercury in the pressure and measuring tubes are equalized, allowing about three inches of the sulfuric acid to one inch of mercury, and the final adjustment obtained by slightly opening the tap on the measuring tube (very slightly), after first adding a little sulfuric acid to the cup, and observing whether the acid runs in or moves up. This must be done with very great care. When accurately adjusted, it should move neither way. Now read off the volume of the NO gas in cc. from the measuring tube. Read also the thermometer suspended near the bulb, and take the height of the barometer in millimeters. The calculation is very simple.

Example Collodion Cotton.

.6 gm. taken. Reading on measuring tube 114.6 cc. NO.
Barometer, 750 mm. Temperature 15° C.

Since 1 cc. NO = .6272 gm. N.,
and correcting for temperature and pressure by the formula $760 \div (1 + d^{15})$ (d = .003665) for temperature of 15° 801.78;

$$\text{then } \frac{114.6 \times 100 \times 750 \times .6272}{801.78 \times .6} = 11.22 \text{ per cent. N.}$$

Theory = 11.11 per cent. for $C_6H_7(NO_2)_3O_5$.

The following is the analysis of a good sample of [illegible] ton suitable for the manufacture of blasting gelatin [illegible]

Soluble cotton	[illegible] per cent	Nitrogen	[illegible]
Gun cotton	[illegible]	Total ash	[illegible]
Non-nitrated cotton	[illegible]		

The nitrogen in nitro-glycerin may of course be determined the nitrometer, but in this case it is better to take a much smaller quantity of the substance, from [illegible] to [illegible] gm is quite sufficient. This will give from 30 to 60 cc of gas and therefore a [illegible] tube without a 100 cc bulb must be used.

Example

[illegible] gm Nitro-glycerin taken. Barometer [illegible] mm. Temperature [illegible] gave [illegible] cc NO

[illegible] per cent N

[illegible]

Theory for $C_3H_5(ONO_2)_3$ [illegible] per cent

[illegible]

SULFUR DETERMINATIONS BY DIFFERENT METHODS

[illegible]

For the purpose of determining which of the methods generally employed in the determination of sulfur in coal is the most [illegible] must analyze [illegible] results the Chemist in Charge of the [illegible] prepared samples of [illegible] bituminous coal [illegible] market as "Castle" from [illegible] the principal [illegible] the United States and Canada [illegible] requesting them to [illegible] methods [illegible] to the method they [illegible] results [illegible] were [illegible] [illegible] results [illegible] [illegible] the method [illegible] [illegible]

	Per cent. Sulfur.
a. Aqua regia method	.005
b. Absorption and oxidation with bromin, insoluble residue treated with aqua regia, and barium sulfate precipitate weighed	.008
c. Absorption and titration with standard iodin solution	.009
d. Method not given	.010
e. Absorption in alkaline solution of nitrate of lead, and weighing the precipitate of barium sulfate	.011
f. Aqua regia method, allowing the solution, after adding barium chlorid, to stand 24 hours	.012
g. Aqua regia method	.012
h. Absorption in potassium permanganate solution and weighing the precipitate of barium sulfate	.013
i. Absorption in cadmium solution and titrating with standard solution of iodin	.013
j. Absorption in potassium permanganate solution and weighing the barium sulfate precipitate	.013
k. Aqua regia method, neutralizing with ammonia preparatory to precipitating the barium sulfate, and allowing to stand 14 hours	.013
l. Absorption in cadmium chlorid, and titrating with standard solution of iodin	.015
m. Absorption and titration with standard solution of iodin	.017
n. Absorption in potassium permanganate solution and weighing the barium sulfate	.017
o. Volumetrically details not given	.019
p. Absorption in cadmium sulfate and titration with standard solution of iodin	.020
q. Aqua regia method	.021
r. Absorption in caustic soda solution and titration with standard solution of iodin	.022
s. Aqua regia method	.024

From the above determinations, there is no apparent advantage of any one method over the others, the same methods yielding

opposite results in different hands. The greatest [illegible] per cent. of sulfur reported are those obtained [illegible] method. This should not be the case. As it [illegible] importance to know the exact amount of sulfur in [illegible] iron, I have been employing both the methods [illegible] permanganate of potash, finally weighing the [illegible] and the "aqua regia method" on the sample, [illegible] rapid work is required and the insoluble residue [illegible] the absorption in cadmium chlorid and [illegible] method. It is the exception when sulfur determ[illegible] two methods disagree. The chief sources of [illegible] regia method are, assuming that the reagents are [illegible]

1. The carrying of the evaporation prepara[illegible] of the graphite and silicon too far, thereby forming [illegible] salts, containing sulfur, and insoluble in dilute acid.

2. The precipitation of barium sulfate in a [illegible] thereby retarding the precipitation very materia[illegible] is the practice to let stand only 12 to 24 hours [illegible] liable to follow.

3. By precipitating the barium sulfate in a [illegible] solution, thereby allowing [illegible] sulfates.

These conditions which [illegible] the solution [illegible] the graphite [illegible] This evaporation [illegible]

THE ANALYSIS OF CYLINDER DEPOSITS.

By Thos. B. Stillman.

The deposits in steam cylinders, formed by the decomposition of lubricating oils, may be classified as simple or compound, depending upon whether the deposit is due to the decomposition of the oil alone or if foreign matters, carried over in the steam from the boilers, are also present.

In the former case, carbon, hydrocarbons, oils, and iron oxid are the principal constituents, whereas, in the latter, oleate of lime, carbonate of lime, and silica are often present in addition to the former.

The following analysis of a sample from a locomotive cylinder would indicate a simple deposit.

Moisture		2.28	per cent.
Oils soluble in ether	Animal	10.54	"
	Mineral	11.23	"
Hydrocarbons insoluble in ether		47.97	"
Fixed carbon		23.73	"
Iron oxid FeO		2.83	"
Undetermined		1.42	"
Total		100.00	"

And the one given below, of a deposit from the steam cylinders of a large stationary engine, would show that scale forming material from the boilers had become a component.

Moisture		13.12	per cent.
Oils soluble in ether	Animal	8.15	"
	Mineral	7.86	"
Soap		2.10	"
Hydrocarbons insoluble in ether		1.67	"
Fixed carbon		2.71	"
Oxids of iron (and aluminum)		6.81	"
Silica		3.65	"
Carbonate of lime		43.22	"
Carbonate of magnesia		10.17	"
Undetermined		0.44	"
Total		100.00	"

In many samples, I have found copper and zinc in the deposits formed by the corrosive action of the liberated oleic acid from animal oil upon the brass or composition bearings.

This corrosive action is very marked where a poor quality of lubricating oil, composed of animal or vegetable oil is used, whereas, a pure neutral mineral oil has no acid action at steam temperature. Oftentimes the statement has been made to me, when a deposit was given for analysis, "All of our lubricating oil is pure mineral oil; we use no other." And yet, upon analysis, lard would be shown in comparatively large amounts.

This is accounted for from the fact that while the consumer believes he is using pure mineral oil, which was sold to him as such, the manufacturer has introduced from [illegible] to [illegible] per cent of [illegible] oil.

A large majority of the so-called "pure mineral" lubricating oils for cylinder use contain at least [illegible] per cent of [illegible], it is the exception and not the rule to find a pure mineral oil for cylinder lubricating purposes.

An analysis of a deposit from the steam cylinder of a large [illegible] steamer gave as a result:

Moisture		[illegible]
Oils soluble in ether	Animal	[illegible]
	Mineral	[illegible]
Fixed carbon		[illegible]
Copper		[illegible]
Iron oxide		[illegible]
Undetermined		[illegible]
Total		[illegible]

Pure mineral lubricating [illegible] was supposed by the [illegible] vessel to be the only lubricant used [illegible] [illegible] taken [illegible] [illegible]

Th[illegible]

T[illegible]

results in different products. That is to say, while the copper when present has generally been estimated as copper oxid, the iron may exist only as oxid or as metallic iron, or both.

No doubt the oleic acid acts to form salts of these metals, but it is certain, in many instances, that when formed, they are immediately decomposed or partially so, and a resulting mixture formed that is somewhat difficult of analysis.

In the analysis here given, it will be noticed that the iron was found both as metal and as oxid.

Moisture		3.77	per cent.
Oils soluble in ether	Animal	21.27	"
	Mineral	19.60	"
Soap		traces	
Fixed carbon		10.90	"
Iron oxid (FeO)		14.01	"
Iron		27.85	"
Lead oxid		0.82	"
Copper oxid		1.07	"
Undetermined		0.71	"
Total		100.00	"

The evolution of hydrogen by HCl, from the deposit, after all oils and fatty substances had been removed, indicated the presence of metallic iron, and the analysis of the residue, after the combustion of the fixed carbon, gave figures by which the ratio of Fe and FeO could be determined. A portion of the deposit, after extraction of oils by ether, is dried, then weighed, the hydrocarbons driven off by heat, and the amount of fixed carbon present converted by combustion with $H_2SO_4 + CrO_3$ into CO_2 and weighed, this weight being calculated back to carbon.

Another portion of the same residue is ignited in a platinum crucible until the carbon is all consumed, then weighed. If the amount of carbon found is small and iron large, this weight may be larger than the original weight of the residue taken, owing to oxidation of metallic iron to Fe_2O_3.

Knowing the weight of carbon, and by making a determination of iron in another sample before ignition, the amount of FeO is easily found.

Scheme for Analysis of Cylinder Deposits

[illegible]

[illegible]

Where qualitative analysis has shown the deposit to be a simple one, the analysis can be stated as follows:

Moisture	———	per cent.
Oils soluble in ether { Animal	———	"
Oils soluble in ether { Mineral	———	"
Hydrocarbons insoluble in ether	———	"
Fixed carbon	———	"
FeO	———	"
Fe	———	"
Total	———	"

For a complex deposit, the following form can be used:

Moisture	———	per cent.
Oils soluble in ether { Animal	———	"
Oils soluble in ether { Mineral	———	"
Soap	———	"
Hydrocarbons insoluble in ether	———	"
Fixed carbon	———	"
Fe	———	"
FeO	———	"
CuO	———	"
PbO	———	"
ZnO	———	"
CaO	———	"
MgO	———	"
CO_2	———	"
SO_3	———	"
Silica, etc.	———	"
Total	———	"

Where the CaO and MgO exist in amounts more than necessary to combine with the CO_2 and SO_3 present, the excess may have united with oleic acid to form soaps insoluble in water, but soluble in ether.

In some instances the PbO and ZnO will be found only in the ether soap solution (3), as lead and zinc oleates, but in others, while they undoubtedly first existed as oleates, they had become decomposed, and the lead and zinc oxides would be found in section (8) of the above scheme.

LABORATORY OF ANALYTICAL CHEMISTRY,
STEVENS INSTITUTE OF TECHNOLOGY.

TESTING A BURETTE

BY H. [illegible]

The usual directions given for testing the accuracy of the calibration marks on a burette are brief and lack details. This [illegible] is considered to be so simple that an extended description is not needed. Most of our authors on chemical analysis are [illegible] to mention the necessity of determining the correctness of the volumetric apparatus, and the usual directions are to weigh the water which the graduate contains. No specifications regarding either the weighing or the water are made except sometimes an [illegible] to a correction for temperature. Thanks to the carefulness of the manufacturers, graduated glassware is ordinarily much more correct than these brief directions would discover. Sometimes however, it becomes necessary to learn the exact quantity or the accuracy of a burette or other graduate, and on such occasions a proper method of determining these facts is a desideratum. In any case, if the testing is necessary, it would seem [illegible] the work properly or not at all.

Were it not for the changes in volume of all matter due to heat, the simple weighing of the water would suffice. But in the first place our burette on account of its [illegible] temperature [illegible] part of its volume for every degree [illegible] is supposed to change [illegible] and we have worked in poorly heated [illegible] where [illegible] for temperature was not allowed [illegible] and the summer [illegible] over [illegible] the change in capacity of other flasks [illegible] This necessitates the selection of a [illegible] at which our instrument should be correct. Most makers [illegible] as the standard temperature and many [illegible] marked. But we may prefer to take a somewhat higher [illegible] temperature [illegible] working temperature [illegible] temperature [illegible]

If [illegible] temperature [illegible] standard [illegible]

tion, "The kilogramme is the vacuum weight of 1000 cc. of water at its temperature of maximum density, about 4°." Reversing this, the volume occupied by 1 kilo of water at 4° (weighed in vacuo) is the volume of 1000 cc. or 1 liter. Since we are obliged to weigh in air and for convenience at temperatures greater than 4°, we can only arrive at the correct liter by knowing the conditions of our experiment and making the proper corrections therefor.

To avoid the imaginary difficulties of making these corrections, several arbitrary standards have been proposed by various authorities, all based upon the volume of 1 kilo of water as weighed in air and at the ordinary laboratory temperatures. The exact temperature selected has been as varied as its author, and none of them possess any essential merit. The tendency is to mislead, since by their use in the conversion of known volumes into weight from the tabular weight of 1 liter of any substance in question, we may fall into an error amounting to one-half per cent. The true liter is independent of the expansion of water by heat, and out of respect for the the authors of the metric system, as well as from a regard for uniformity, it may well be retained as our actual standard.

Our first correction depends upon the variation in the weight of 1 liter of water under a change of temperature. This has been determined by several experimenters, and a careful comparison of their best results will give us a very accurate table. The following has been compiled from the latest determinations, plotted into a curve of expansion and corrected by the method of second differences. (See Table I.)

At our standard temperature, 25°, the true weight of 1 liter of water is seen to be 997.27 gms. The apparent weight of 1 liter of water at 25° as weighed with brass weights in air at the same temperature and at 760 mm. barometric pressure, would be less than this by an amount equal to the weight of air displaced by the difference in volume between the water and the weights. With brass at a sp. gr. of 8, and water at 1, the difference in volume equals 7/8 of the volume of the water or 7/8 of 1 liter. 1 liter of air at 25° and 760 mm. B. weighs 1.1845 gms. and 7/8 of this 1.0364 gms. Hence the liter under these circumstances weighs or at least counterbalances weights equal to 996.23 gms. This correction for loss

TABLE NO. 1.

Temperature.	Density or Grams in 1 Liter.	Volume or Centimeters cu. in 1 Kilo.	Temperature.	Density or Grams in 1 Liter.	Volume or Centimeters cu. in 1 Kilo.
C°.			C°.		
0	999.86	1000.14	51	987.29	1012.71
1	999.91	1000.09	52	986.78	1013.22
2	999.95	1000.05	53	986.26	1013.74
3	999.98	1000.02	54	985.73	1014.27
4	1000.00	1000.00	55	985.19	1014.81
5	999.97	1000.03	56	984.64	1015.36
6	999.94	1000.06	57	984.09	1015.91
7	999.90	1000.10	58	983.53	1016.47
8	999.85	1000.15	59	982.96	1017.04
9	999.79	1000.21	60	982.38	1017.62
10	999.72	1000.28	61	981.79	1018.21
11	999.64	1000.36	62	981.19	1018.81
12	999.55	1000.45	63	980.58	1019.42
13	999.44	1000.56	64	979.97	1020.03
14	999.32	1000.68	65	979.35	1020.65
15	999.19	1000.81	66	978.73	1021.27
16	999.05	1000.95	67	978.10	1021.90
17	998.90	1001.10	68	977.46	1022.54
18	998.74	1001.26	69	976.81	1023.19
19	998.57	1001.43	70	976.15	1023.85
20	998.38	1001.62	71	975.48	1024.52
21	998.18	1001.82	72	974.81	1025.19
22	997.97	1002.03	73	974.13	1025.87
23	997.74	1002.26	74	973.44	1026.56
24	997.51	1002.49	75	972.74	1027.26
25	997.27	1002.73	76	972.04	1027.96
26	997.02	1002.98	77	971.33	1028.67
27	996.76	1003.24	78	970.61	1029.39
28	996.48	1003.52	79	969.89	1030.11
29	996.19	1003.81	80	969.16	1030.84
30	995.89	1004.11	81	968.42	1031.58
31	995.58	1004.42	82	967.68	1032.32
32	995.25	1004.75	83	966.93	1033.07
33	994.92	1005.08	84	966.18	1033.82
34	994.58	1005.42	85	965.42	1034.58
35	994.23	1005.77	86	964.65	1035.35
36	993.87	1006.13	87	963.87	1036.13
37	993.50	1006.50	88	963.09	1036.91
38	993.12	1006.88	89	962.30	1037.70
39	992.73	1007.27	90	961.51	1038.49
40	992.32	1007.68	91	960.71	1039.29
41	991.91	1008.09	92	959.91	1040.09
42	991.49	1008.51	93	959.10	1040.90
43	991.05	1008.95	94	958.29	1041.71
44	990.61	1009.39	95	957.47	1042.53
45	990.16	1009.84	96	956.65	1043.35
46	989.70	1010.30	97	955.82	1044.18
47	989.23	1010.77	98	954.99	1045.01
48	988.76	1011.24	99	954.15	1045.85
49	988.28	1011.72	100	953.30	1046.70
50	987.79	1012.21			

of weight in air varies with the barometer, but for any pressure between 730 and 780 mm. a change of less than .05 cc. per liter is occasioned, which for our purpose may be entirely disregarded. The temperature of the air will be approximately the same as that of the water, a maximum difference of 5° modifying the result by only .02 cc. per liter, and by subtracting the correction from the previous table we get the following:

TABLE NO. 2.

Apparent Weight of 1 Liter of Water at Different Temperatures, as Weighed with Brass Weights in Air.

Temperature of Water.	Apparent Weight.	Temperature of Water.	Apparent Weight.
C°.		C°.	
15	998.1	28	995.4
16	998.0	29	995.2
17	997.8	30	994.9
18	997.7	31	994.6
19	997.5	32	994.2
20	997.3	33	993.9
21	997.1	34	993.6
22	996.9	35	993.2
23	996.7	36	992.9
24	996.5	37	992.5
25	996.2	38	992.1
26	996.0	39	991.7
27	995.7	40	991.3

This table at 25° gives the apparent weight of 1 liter of water as measured by our burette. The expansion or contraction of the glass above or below this temperature will modify the other figures by an amount equal to .023 cc. for each degree, and this amount must be subtracted below 25°, and added above 25°, to the figures of the table. Hence we have a final table giving the apparent weight of 1 liter of water under ordinary circumstances as above stated. As most of our volumetric glassware is marked as standard at 15°, we give a table for this temperature also, although the difference amounts to only .02 per cent.

Table No. 3

Apparent Weight of 1 Liter of Water at Different Temperatures as Weighed with Brass Weights in Air (Corrected for Expansion of Glass)

Temperature	Apparent Weight		Apparent Volume	
C	Standard at 15°	Standard at 20°	Standard at 15°	Standard at 20°
15	[illegible]	[illegible]	[illegible]	[illegible]
16	[illegible]	[illegible]	[illegible]	[illegible]
17	[illegible]	[illegible]	[illegible]	[illegible]
18	[illegible]	[illegible]	[illegible]	[illegible]
19	[illegible]	[illegible]	[illegible]	[illegible]
20	[illegible]	[illegible]	[illegible]	[illegible]
21	[illegible]	[illegible]	[illegible]	[illegible]
22	[illegible]	[illegible]	[illegible]	[illegible]
23	[illegible]	[illegible]	[illegible]	[illegible]
24	[illegible]	[illegible]	[illegible]	[illegible]
25	[illegible]	[illegible]	[illegible]	[illegible]
26	[illegible]	[illegible]	[illegible]	[illegible]
27	[illegible]	[illegible]	[illegible]	[illegible]
28	[illegible]	[illegible]	[illegible]	[illegible]
29	[illegible]	[illegible]	[illegible]	[illegible]
30	[illegible]	[illegible]	[illegible]	[illegible]
31	[illegible]	[illegible]	[illegible]	[illegible]
32	[illegible]	[illegible]	[illegible]	[illegible]
33	[illegible]	[illegible]	[illegible]	[illegible]
34	[illegible]	[illegible]	[illegible]	[illegible]
35	[illegible]	[illegible]	[illegible]	[illegible]
36	[illegible]	[illegible]	[illegible]	[illegible]
37	[illegible]	[illegible]	[illegible]	[illegible]
38	[illegible]	[illegible]	[illegible]	[illegible]
39	[illegible]	[illegible]	[illegible]	[illegible]
40	[illegible]	[illegible]	[illegible]	[illegible]

This table is accurate to probably [illegible] per cent which is about the limit of error in an [illegible] burette [illegible]

In testing a burette or other graduate the [illegible] ation should be as nearly as possible the same as that [illegible] use. The burette should be used after a lapse of [illegible] time of an ordinary titration. We have found that [illegible] burette on draining the contents out rapidly the [illegible] down to the [illegible] was

[illegible]

Water, acid and salt solutions about the same, but alkalies a little more slowly. As a careful titration takes usually more than 2 minutes and less than 15, we are accustomed to read the burette after 5 minutes standing.

Select water at the same temperature as the balance room. A convenient vessel for holding the water while weighing is a good-sized weighing bottle or a glass-stoppered 100 cc. flask. A solution of bichromate of potash in moderately strong sulphuric acid used warm is an excellent agent for removing grease or other foreign matter from a burette tube.

The following example of 2 burettes purchased recently will show the method of testing and also exhibit the quality of graduated glass-ware to be found in the market. With two or three tested burettes and flasks in a laboratory we may readily compare others and make them equivalent.

25 cc. Burette. Mark B. Water at 25°.

	Weighings.	H_2O.	True cc.	Burette.	Difference.
Empty	25.120			0.00	
	32.931	7.811	7.84	7.82	7.82
	41.452	8.521	8.55	16.37	8.55
	49.252	7.800	7.83	24.21	7.84
			24.22		

Same burette again for total capacity. Water at 25°.

	Weighings.	Burette.	
Empty	25.084	0.00	
	49.946	24.94	
	24.862 = 24.96 cc.		error, .02 cc.

Duplicate. Water at 25°.

		Burette.	
Empty	25.086		
	49.983	0.00	
	24.897 = 25.00 cc.	24.97	error, .03 cc.

Burette readings were taken to [illegible], but the error [illegible] such reading would amount to probably [illegible]. The results of the above test show the burette to be highly accurate. It will be noticed that duplicate determinations give concordant results, the variations being less than the probable error of any single reading. This fact alone will indicate the general accuracy of the method.

[illegible] Burette Made A [illegible]

	Weighings	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Empty	[illegible]			[illegible]			
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]			[illegible]
Empty	[illegible]						
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]

[illegible]

The test points to a probable [illegible] in the [illegible] of the burette. This fact was proved by a duplicate [illegible] for the lower part of the [illegible] and the [illegible] of this burette with the [illegible] burette marked [illegible] of [illegible] was discovered between the [illegible]. An examination of the [illegible] showed that the [illegible] of the burette [illegible] the [illegible] and that the [illegible] the [illegible] [illegible]

A METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. Browning.

At the suggestion of Prof. F. A. Gooch, and following the general mode of procedure laid down in his paper† upon the separation of sodium and potassium from lithium by the action of amyl alcohol on the chlorids, I undertook a series of experiments looking toward the separation of strontium from calcium by the action of amyl alcohol on the nitrates. On boiling several portions of the so-called chemically pure calcium and strontium nitrates with amyl alcohol, nearly complete solubility was observed in case of the calcium salt, while corresponding insolubility seemed to be characteristic of the strontium salt, and these results seemed to warrant proceeding with the work.

For the quantitative tests to be described standard solutions of specially purified strontium and calcium nitrates were prepared. In general the preparation was effected by precipitating a soluble salt of either element with ammonium carbonate in the presence of ammonium chlorid, washing thoroughly with boiling water, dissolving in the least possible amount of nitric acid, and making up to measure. In the earlier experiments other methods of purification were used, such as the precipitation of the strontinum nitrate by alcohol, and in case of the calcium salt the preparation of the nitrate from the carbonate precipitated by ammonium carbonate from a solution of calcium sulfate. The method first described, however, gave satisfactory results, the spectroscope failing to show in the product thus obtained any trace of intermixture of calcium and strontium salts, or the presence of any other appreciable impurity. In the determination of the standard of these solutions definite amounts were drawn off from burettes into counterpoised beakers or crucibles (according as the method of determination was by precipitation or evaporation) and weighed as a check on the burette reading. The strontinum nitrate in each portion was converted into the sulfate either by precipitation in the presence of alcohol, or by evaporating and igniting, these methods yielding results closely agreeing. The calcium was determined by evaporation with sulfuric acid. The first series of experiments was directed

*Am. Jour. Sci., Jan., 1892.
†Am. Chem. Jour., vol. ix, p. 33.

toward an investigation of the action of amyl alcohol upon strontium nitrate alone. Accordingly several amounts of the strontium salt were measured from a burette into counterpoised [illegible] beakers of about [illegible] cc. capacity, and weighed. The water was then evaporated over a water bath, and the dry salts [illegible] a few drops of water and boiled with [illegible] cc. of amyl alcohol, that amount being determined upon for convenience. Care should be taken not to add more than the necessary amount of water to dissolve the salt, inasmuch as the presence of much water delays the process, it being necessary to expel all the water before the amyl alcohol can do its work, and tends to cause spattering from the superheating of the water and consequent sudden generation of steam under the alcohol. It has been my experience that in the presence of a few drops of water the boiling goes on quietly, the water escaping easily through the amyl alcohol, and in the course of a few minutes the alcohol reaches its normal boiling temperature, 128–130° C. In order that the inflammable vapors of the alcohol might not reach the flame during the boiling, the beaker was placed upon a piece of asbestos board [illegible] square. When the temperature of the alcohol reached its normal boiling point, 128–130° C., as shown by a thermometer, the beaker was removed and the strontium nitrate filtered off upon an asbestos felt in a perforated platinum crucible, the crucible and felt having been previously dried and weighed.

The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell-glass [illegible] glass plate. The last traces of strontium nitrate were removed from the beaker by washing with small amounts of pure [illegible] boiled amyl alcohol, introduced in a wash bottle, the mouth piece of which consisted of a small [illegible] tube passing through the stopper and drawn out and plugged at the lower end [illegible] so that the [illegible] salt is not [illegible]. So this device the [illegible] from [illegible] into the amyl alcohol [illegible]. The crucible containing the strontium nitrate was [illegible] washed [illegible] alcohol [illegible] and [illegible]. A constant weight was [illegible] [illegible] minutes. The following table gives the results [illegible] percent of the strontium [illegible] calculated as oxid.

Series I.

(1)	SrO taken 0.1229 gm.	SrO found 0.1220 gm.	Loss 0.0009 gm.
(2)	" " 0.1231 "	" " 0.1221 "	" 0.0010 "
(3)	" " 0.1230 "	" " 0.1219 "	" 0.0011 "
(4)	" " 0.1227 "	" " 0.1213 "	" 0.0014 "

These results suggested a possible solubility of the strontium salt, and, accordingly, experiments were made to test this point. Amounts of strontium nitrate closely agreeing with those above were taken and treated in the same manner. The filtrates amounting, without the washings, to about 25 cc. were evaporated to dryness. The residue was ignited to burn off organic matter from the amyl alcohol, treated with sulphuric acid, heated to low redness, and weighed. In two cases the residue of strontium sulfate was found to contain of the oxid respectively 0.0009 gm. and 0.0010 gm. As will be seen the solubility of the strontium nitrate averages about 0.0010 gm. of the oxid to 30 cc. of amyl alcohol used. The exact extent of this solubility depends, of course, upon the amount of amyl alcohol remaining after boiling; and since the source of heat is removed as soon as the normal boiling temperature of the alcohol is reached, very little decrease in the volume of the previously boiled alcohol results. On measuring the amounts of the alcohol remaining in several experiments I found them to approximate closely to 25 cc. It seemed justifiable, therefore, to add as a correction to the apparent amount of strontium oxid found 0.0010 gm. for every 25 cc. of amyl alcohol remaining, or for every 30 cc. originally taken. Experiments were also made to determine whether the strontium nitrate might have been at all broken down in the process of boiling and heating so that some strontium might be present in the final residue in the form of oxid or nitrite. In two of these experiments portions of strontium nitrate left by the treatment with amyl alcohol were dissolved, precipitated as the sulfate and weighed as such, and the results of these experiments (5 and 6) go to show that the composition of the strontium nitrate is not appreciably changed in the process of separation and drying. In certain other experiments directed to the same end, the residues of the process of separation were, after weighing and drying, treated with a drop of nitric acid, and again dried at 150° C. and weighed. These tests (7) and (8) confirm the indications of the previous experiments. Finally a

third experiment was made upon strontium nitrate dried at [illegible] C to see what decomposition might result by heating to temperatures somewhat higher than 150° C the temperature at which the residues of the previous experiments had been dried The result shows that the loss in the twenty five degrees above 150° C is exceedingly slight

5	$Sr(NO_3)_2$ calculated as SrO	[illegible]
	The same dissolved and precipitated as $SrSO_4$, calculated as SrO	[illegible]
6	$Sr(NO_3)_2$ calculated as SrO	[illegible]
	The same dissolved and precipitated as $SrSO_4$, calculated as SrO	[illegible]
7	$Sr(NO_3)_2$ calculated as SrO	[illegible]
	The same dried at 150° C after adding a drop of HNO_3	[illegible]
8	$Sr(NO_3)_2$ calculated as SrO	[illegible]
	The same dried at 150° C after adding a drop of HNO_3	[illegible]
9	Weight of $Sr(NO_3)_2$ dried at 150° C	[illegible]
	Weight of the same portion fused at 250° C	[illegible]
	Weight of the same portion fused at 250° C	[illegible]

When calcium nitrate was treated in a similar manner [illegible] ing with amyl alcohol the mass of the salt dissolved [illegible] portions separated out on the bottom or sides of the beaker [illegible] residues were however very small and on weighing were [illegible] to several [illegible] gm or [illegible] gm of the salt In several [illegible] this insoluble residue was washed thoroughly with [illegible] dissolved in water tested before the spectroscope and [illegible] the characteristic calcium spectrum All experiments [illegible] the fact that the formation of the residue was due [illegible] slight change of composition of the calcium nitrate [illegible] occasions the water in which the residue appeared [illegible] drop of extremely dilute solution of potassium permanganate and this action suggested the presence of a nitrite Treatment [illegible] residue with [illegible] subsequent evaporation [illegible] of a dilute solution of the calcium salt [illegible] dissolved [illegible]

It is [illegible] that the residue [illegible] amyl alcohol [illegible] separately [illegible] calcium salt [illegible] the residue were [illegible]

small that it was not practicable to solve this question, at once, exactly and satisfactorily without directing attention too far from the main issue. Moreover, the error introduced by this peculiar behavior of the calcium salt proved to be insignificant in its effects upon the quantitative determination of the calcium, and accordingly, it was disregarded in the subsequent tests.

The next experiments were directed toward a separation of strontium and calcium nitrates. Definite amounts of a solution of strontium nitrate were measured from burettes into counterpoised beakers and weighed, as already described, the calcium nitrate was then added in solution, and the weight taken again. The water was evaporated and the dry salts dissolved again in the least possible amount of water and boiled with amyl alcohol (30 cc.), as before. The strontium was filtered off into a perforated platinum crucible containing an asbestos felt, dried and weighed as previously described. The calcium was determined in the form of the sulfate, by evaporation of the alcohol, treatment with an excess of sulfuric acid, and ignition.

Correction was made for the solubility of the strontium nitrate, and its consequent presence with the calcium, by calculating the amount dissolved in the portion of amyl alcohol employed to the condition of sulfate and subtracting that quantity from the apparent amount of calcium sulfate found. The results of this mode of proceeding are recorded in experiments (10) and (11).

	SrO Taken.	SrO Found. (Corrected.)	Error.	CaO Taken.	CaO Found. (Corrected.)	Error.
(10)	0.0911 gm.	0.0932 gm.	0.0021 gm.	0.0932 gm.	0.0907 gm.	0.0025 gm.—
(11)	0.0915 "	0.0945 "	0.0030 "	0.0933 "	0.0899 "	0.0034 " —

After making the correction in the manner specified it is evident that the amount of strontium indicated is greater than that originally taken. It is apparent, therefore, that the strontium nitrate must have been contaminated, probably mechanically, by the calcium salt, as the calcium salt is found to be correspondingly deficient in amount. It was thought best, therefore, to have recourse to a double treatment with the alcohol. Accordingly after the first boiling already described the alcohol carrying the greater part of the calcium in solution was decanted upon an asbestos felt under the conditions previously described and collected in a beaker placed

to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water treated with a drop of nitric acid to assure the condition of nitrate and evaporated to dryness. After dissolving in a few drops of water 30 cc. of alcohol were added, and the boiling repeated. The residue was filtered off upon the same felt through which the first portion had been decanted, and washed with amyl alcohol, care being taken to remove all particles of the residue from the beaker by careful rubbing. The crucible and residue were heated in an air bath at 150° C. as before, and then weighed. The filtrate from the two treatments and the washings were treated differently in the two series of experiments. In Series II, the filtrate was precipitated with sulfuric acid, ethyl alcohol being added to secure thorough [illegible]. The precipitated sulfate was filtered off upon asbestos, heated to low redness and weighed. In Series III the alcoholic filtrate was evaporated to a small volume, transferred to a weighed platinum crucible and evaporated. The residue was ignited to [illegible] organic matter, treated with sulfuric acid and again ignited to low redness and weighed.

Series II.

	SrO taken	[illegible]	Error	CaO taken	[illegible]	[illegible]
12	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
13	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
15	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Series III.

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

The [illegible]

series is less than 0.0001 gm. + on the oxid; that of the calcium amounts to 0.0017 gm. — on the oxid in Series II. and to 0.0005 gm. — in Series III.

In both processes the correction for the solubility of strontium nitrate in amyl alcohol, determined as previously described, was applied— 0.0020 gm. being added to the weight of the strontium oxide found after the double treatment with amyl alcohol, and 0.0035 gm. being deducted from the apparent weight of the calcium sulfate found before calculating it to the form of the oxid. The latter of the two processes, which are identical so far as handling of the strontium is concerned, yields the better results in the determination of the calcium, doubtless because a trifling amount of calcium sulfate remains in solution in the filtrate in the former process, while in the latter every trace should be recovered. The deposition of minute traces of calcium in the precipitation of the strontium nitrate, to which reference has been previously made, is evidently a matter of no signifiance in comparison with the ordinary errors of manipulation.

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

BY P. E. BROWNING.

The fact that strontium can be separated quantitatively from calcium by boiling the nitrates with amyl alcohol, as I have recently shown† naturally suggested a similar separation of barium from calcium by the same general treatment. Solutions of specially purified barium and calcium nitrates were prepared and standardized, either by the evaporation or filtration of definite portions after treatment with sulfuric acid. The mean of several closely agreeing results, both by evaporation and filtration, was taken as the standard. The method followed was essentially the same as described in the method for the quantitative separation of strontium from calcium referred to above. The first series of experiments was directed toward an investigation of the action of amyl alcohol upon barium nitrate alone. Accordingly definite amounts of the barium salts were measured into Bohemian beakers of about 100 cc. capacity and weighed. The water was then evap-

*Am. Jour. Sci. Apr. 1892.
†See preceding paper.

orated over a water bath, and the dry salts dissolved [illegible] of water and boiled with 30 cc. of amyl alcohol, that [illegible] determined upon as convenient, until the normal [illegible] the alcohol was reached (128 to 130° C.). During the [illegible] beaker was placed upon a piece of asbestos board [illegible] square to keep the inflammable fumes of the alcohol [illegible] flame. When the temperature of the alcohol reached [illegible] boiling point the beaker was removed and the barium [illegible] tered off upon an asbestos felt in a perforated platinum [illegible] crucible and felt having been previously dried and weighed. The filtration was carried on under gentle pressure, the filtrate being received in a beaker standing under a bell jar upon a glass plate. The last traces of barium nitrate were removed from the beaker by washing with small amounts of anhydrous [illegible] contained in a wash bottle previously described, to the [illegible] of which a small chloride of calcium tube was connected. The crucible containing the barium nitrate was placed in [illegible] and heated to 150° C. The process of heating and weighing was repeated until a constant weight was obtained. Series [illegible] gives the results of these experiments, the barium being calculated [illegible]

Series [illegible]

	[illegible]	[illegible]	[illegible]
1	[illegible]	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]
3	[illegible]	[illegible]	[illegible]
4	[illegible]	[illegible]	[illegible]

These results show plainly enough the complete [illegible] the barium salt in the amyl alcohol. Nitrates [illegible] filtrates of 3 and 4 were evaporated to dryness [illegible] off any organic matter from the amyl alcohol [illegible] ture and heated to 150° to dryness and weighed. The weights in both cases showed the [illegible] residue.

Series [illegible]

	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Series III.

	BaO Taken. Gms.	BaO Found. Gms.	Error. Gms.	CaO Taken. Gms.	CaO Found. Gms.	Error. Gms.
10.	0.1304	0.1308	0.0004+	0.0927	0.0921	0.0006—
11.	0.1043	0.1046	0.0003+	0.0371	0.0370	0.0001—
12.	0.1037	0.1036	0.0001—	0.0743	0.0744	0.0001+
13.	0.0783	0.0776	0.0007—	0.0427	0.0422	0.0005—
14.	0.0519	0.0521	0.0002+	0.0369	0.0361	0.0008—
15.	0.0519	0.0512	0.0007—	0.0570	0.0567	0.0003—
16.	0.0261	0.0259	0.0002—	0.0925	0.0925	0.0000

The next experiments were directed toward a separation of barium and calcium nitrates. Definite amounts of a solution of barium nitrate were measured from burettes into counterpoised beakers and weighed, as already described, the calcium nitrate was then added in solution and the weight taken again. The water was evaporated and the dry salts dissolved again in the least possible amount of water, and boiled as before with 30 cc. of amyl alcohol. The barium salt was filtered off into a perforated platinum crucible containing an asbestos felt, dried and weighed as previously described. The calcium was determined in the filtrate, in the form of the sulfate, by evaporation of the alcohol, treatment with an excess of sulfuric acid and ignition. Series II gives the result of this treatment.

In Series III the effect of a double treatment with the alcohol is recorded. In these experiments, after the first boiling, already described, the alcohol was decanted upon an asbestos felt, under the conditions previously mentioned, and collected in a beaker placed to receive it. The residue was then dried at a gentle heat over a radiator to remove amyl alcohol, dissolved in a few drops of water, and this solution was treated with a drop of dilute nitric acid to assure the condition of nitrate, and evaporated to dryness. After dissolving in a few drops of water, 30 cc. of alcohol were added, and the boiling repeated. The residue was filtered off upon the felt through which the first portion had been decanted and washed with amyl alcohol, care being taken to remove all particles from the beaker by careful rubbing. The crucible and residue were heated to 150° C. as before and weighed. The results after one treatment are fully as satisfactory as those after the double treatment,—a point which simplifies the method considerably. In the separation of strontium from calcium the double treat-

ment was necessary. The form in which the salts separate suggested a possible explanation. The strontium nitrate separates in plate-like masses, while the barium is much more granular and therefore less liable to include foreign matter.

Series IV contains the results of certain experiments directed toward the separation of barium and strontium together from calcium. Definite portions of the three nitrate solutions were measured into counterpoised beakers and the successive weights taken as previously described. The method of treatment was the same as that described in the double treatment of the barium and calcium salts. The correction for the solubility of the strontium salt was applied (0.001 gm. of strontium oxid to 30 cc. of the alcohol used) in the manner defined in the paper upon the separation of strontium from calcium. The results are tabulated for the nitrates in the cases in which barium and strontium were treated together, but the errors are also averaged on the oxids for the amounts of barium and strontium nitrates taken in order that they may be compared more conveniently with the results of the previous series.

Series IV.

	$Ba(NO_3)_2$ and $Sr(NO_3)_2$ taken. Gms.	$Ba(NO_3)_2$ and $Sr(NO_3)_2$ found and corrected. Gms.	Error in nitrates. Gms.	Error Averaged and calculated as oxid. Gms.	CaO taken. Gms.	CaO found. Gms.	Error. Gms.
17.	0.3941	0.3945	0.0004+	0.0002+	0.0283	0.0277	0.0006—
18.	0.1436	0.1442	0.0006+	0.0003+	0.0568	0.0558	0.0010—
19.	0.3163	0.3152	0.0011—	0.0006—	0.0284	0.0274	0.0010—
20.	0.1978	0.1978	0.0009—	0.0005+	0.0285	0.0280	0.0005—
21.	0.1948	0.1932	0.0016—	0.0008—	0.0833	0.0835	0.0002+
22.	0.1971	0.1971	0.0000	0.0000	0.0830	0.0817	0.0013—
23.	0.1973	0.1960	0.0013—	0.0007—	0.0830	0.0824	0.0006—
24.	0.1959	0.1970	0.0011+	0.0005+	0.0830	0.0819	0.0011—
25.	0.1971	0.1963	0.0008+	0.0004+	0.0834	0.0831	0.0003—

In experiments (21), (25) 15 cc. of the alcohol were used in each boiling instead of the 30 cc. of the previous experiments, and thus the total amount of the corrections for the solubility of the strontium salt was reduced one half. In experiments (21), (23) and (25) the calcium was determined by precipitation with sulfuric acid, the precipitate being filtered off, ignited at low redness and weighed

The rapidity of execution and satisfactory character of the results of this method of separating barium from calcium seem to place it among good analytical methods.

ON THE QUALITATIVE SEPARATION AND DETECTION OF STRONTIUM AND CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By P. E. Browning.

In a recent paper† I have shown that strontium and calcium may be separated quantitatively by boiling the nitrates of these elements with amyl alcohol and applying the corrections determined for the solubility of the strontium salt. The qualitative separation, however, is somewhat vitiated by the deposition of a slight residue upon the bottom of the test tube or beaker when calcium nitrate is boiled with amyl alcohol. While this deposit weighs but a few tenths of a milligram and is insignificant in its effects upon the interpretation of the quantitative results, it may easily be mistaken for strontium in the qualitative test unless tested spectroscopically. This residue when dried, dissolved in water and nitric acid, and again treated with amyl alcohol is not dissolved completely but again separates out wholly or partially. The possibility of the formation of the calcium salt of an organic acid by the action of the nitric acid on the amyl alcohol (a point to which reference was made in the paper before mentioned), suggested the idea that ignition might so change the residue that it would not re-appear upon a second boiling with the amyl alcohol. Experiment proved the truth of this presumption ; for it was found that after getting the ignited residue into solution with water and a drop of dilute nitric acid, subsequent boiling with amyl alcohol effected complete solution, as shown by experiments (1), (2), (3), (4) of Series I below. In applying the method qualitatively, small amounts of the amyl alcohol may be conveniently used and the boiling carried on in a test tube, care being taken to keep the inflammable fumes of the alcohol from the flame. Five cubic centimeters of the alcohol is a convenient amount to use in each boiling and the error introduced by the solubility of the strontium salt is thus reduced to a minimum, the solubility in 30 cc. having been determined to be 0.001 gm. of the oxid. Experiments made to test the delicacy of the method as regards the detection of strontium alone are recorded in Series I (5), (6), (7), (8), (9) ; and (10), (11), (12), (13), give the results of the treatment in the presence of both strontium and calcium. Into a test tube is put the mixture of the

*Am. Jour. Sci., May, 1892.
†Reprinted in this Number.

nitrates of strontium and calcium not exceeding [illegible] grams, that being the limit of the solubility of calcium nitrate in [illegible] amyl alcohol. After dissolving in a few drops of water [illegible] amyl alcohol are added and the boiling is carried on until the [illegible] boiling point of the alcohol, 128 [illegible] C. is reached. If strontium is present to the amount of [illegible] gram of the oxide [illegible] a decided separation takes place. If the amount is [illegible] be readily distinguished from the residual spots deposited on the bottom of the tube by the calcium salt. The [illegible] the calcium salt dissolved is decanted upon a dry filter [illegible] in a dry funnel and the residue washed in the tube with [illegible] absolute ethyl alcohol, this also being filtered [illegible] taining the amyl alcohol. The filtrate is reserved [illegible] calcium, while the residue, if so small that it may [illegible] posit, is dried gently and finally ignited by agitating [illegible] a flame. After cooling the tube a few drops of water [illegible] of nitric acid are added and the boiling repeated. As [illegible] of Series I show, any amount of strontium [illegible] oxid separates out distinctly, while the slight [illegible] does not reappear. My experience has been that [illegible] cium nitrate equal to [illegible] gram gave a deposit [illegible] about equal to [illegible] gram of strontium oxid [illegible] The residues from the second treatment in Series I [illegible] all dissolved in a few drops of water treated with [illegible] chloric acid and tested [illegible] to the spectroscope [illegible] strontium lines but [illegible] calcium. [illegible] from the first boiling gave [illegible] strontium.

The [illegible] to the experiments of Series II. [illegible]

character of the precipitate in the case of calcium was moreover, distinctive, it being in every case light and flocky, and collecting in floating masses. With the precautions noted very satisfactory results can be obtained by this method, not the least advantage being the rapidity with which a determination can be made. It will be noticed that in some cases calcium and strontium are recorded as the nitrates and in others tabulated as oxids. When either strontium or calcium were used in large quantities the pure nitrate was weighed out directly ; when very small amounts were used these were taken from the standardized solutions of the nitrates used in the quantitative work, the standards of which had been recorded in terms of the oxid. The strontium and calcium salts used in this work were specially purified by the methods detailed in my previous paper.

Series I.

	SrO taken.	$Ca(NO_3)_2$ taken.	Deposit after first boiling.	Deposit after second boiling.
1.		0.1 gm.	Trace	
2.		0.2 "	Slight	None
3.		0.2 "	Slight	None
4.		0.2 "	Distinct	Faintest trace
5.	0.0003 gm.		Faint trace	Faint trace
6.	0.0003 "		Faint trace	Faintest trace
7.	0.0005 "		Distinct	Distinct
8.	0.0005 "		Distinct	Distinct
9.	0.0010 "		Distinct	Distinct
10.	0.0010 "	0.2 "	Distinct	Distinct
11.	0.0005 "	0.1 "	Distinct	Faintest trace
12.	0.0007 "	0.1 "	Distinct	Faint trace
13.	0.0008 "	0.05 "	Distinct	Distinct

Series II.

	$Sr(NO_3)_2$ taken.	CaO taken.	Result.
1.	0.001 gm.		Faint granular cloudiness
2.	0.1 "		" " "
3.	0.2 "		" " "
4.		0.001 gm.	Decided flocky floating masses.
5.		0.0005 "	" " " "
6.		0.0002 "	" " " "
7.		0.0001 "	Plain " " "
8.		0.00005 "	Faint " " "
9.	0.1 "	0.0005 "	Decided " " "
10.	0.1 "	0.0002 "	" " " "
11.	0.1 "	0.0001 "	Plain " " "
12.	0.2 "	0.0002 "	Decided " " "

A METHOD FOR THE DETERMINATION OF BARIUM IN THE PRESENCE OF CALCIUM AND MAGNESIUM.*

By F. W. Mar.

The recent investigation† by Prof. R. Fresenius of the value of the various methods which have been proposed for the separation of barium and calcium, shows that but two of the methods tested by him are sufficiently accurate for good analytical work, and even with these it is necessary to make two treatments in order to obtain a complete separation. The method here described may therefore be of interest and by reason of its rapidity and accuracy may prove valuable, although since the publication of the work of Fresenius another method‡ has been published from this laboratory which, in point of accuracy, leaves little to be desired.

It has long been known that barium chlorid is insoluble to a marked degree in concentrated hydrochloric acid, but the difficulty of filtering off the strong acid has in the past prevented the determination of the exact amount of this insolubility, and for the same reason the reaction has not been available for quantitative use. Since the invention of the Gooch crucible, however, the treatment of such strong acid filtrates has become a matter of the greatest ease, and it seemed worth while to investigate the limits of the insolubility of barium chlorid in the strong acid and to ascertain whether the reaction might not be of use in the separation of barium from calcium and magnesium, the chlorids of which are soluble in the strong acid.

The barium chlorid used in the following experiments was the pure crystallized chlorid containing two molecules of water. The calcium salt was the pure fused chlorid, and the magnesium salt was the pure crystallized magnesium chlorid dried at 50° C. As the two latter were not determined in the experiments it was not necessary to know the composition of the salts used as regards hygroscopic moisture. Attention was first given to determining the solubility of barium chlorid in hydrochloric acid.

*Am. Jour. Sci. June, 1892.
†Zeitschrift für anal. Chem., **30**, 595.
‡P. E. Browning, this Journal, p. 339.

Series A.

Exp.	$BaCl_2 . 2H_2O$ gms.	Water. cc.	HCl. cc.	Total. Filtrate. cc.	$BaCl_2$. gms.	Loss. gms.
1.	0.5024	5	20		0.4241	0.0041
2.	0.5084	5	20		0.4304	0.0030
3.	0.5099	2	25		0.4320	0.0027
4.	0.5033	2	25	90	0.4251	0.0039
5.	0.5047	2	25	52	0.4247	0.0055
6.	0.5065	2	50	115	0.4257	0.0060
7.	0.5008	2	50	75	0.4218	0.0051
8.	0.5011	2	50	93	0.4220	0.0051
9.	0.5024	2	75	123	0.4246	0.0037

The experiments in Series *A* were made as follows: The barium salt was weighed out, placed in a small beaker and dissolved in the amount of water indicated. The barium was then precipitated as the anhydrous chlorid by adding, gradually first, the amount of hydrochloric acid shown. After standing for five or ten minutes the precipitates were filtered off upon asbestos in Gooch crucibles, washed with concentrated hydrochloric acid, dried, sometimes over a low flame (at about 150°–200° C.) and sometimes in an air bath heated to 165° C., and weighed. In several cases the total filtrate was measured and the volume is given in the tabular statement. The results show a considerable solubility amounting to about 1 part in 8000 under the conditions given.

Series B.

Exp.	$BaCl_2 . 2H_2O$ gms.	Water. cc.	HCl. cc.	Total. Filtrate. cc.	$BaCl_2$. gms.	Loss. gms.
10.	0.5057	2	25	75	0.4268	0.0042
11.	0.5017	5	50	90	0.4198	0.0078
12.	0.5068	3	50	100	0.4235	0.0085
13.	0.5019	2	100	144	0.4186	0.0082

The experiments in Series *B* were conducted similarly to those of Series *A* except that the precipitates were allowed to stand 24 hours before filtration. The loss due to solubility was, as is shown by the table, greater than before, due doubtless to the escape of hydrochloric acid gas from the solution.

Series C.

Exp.	$BaCl_2 . 2H_2O$ gms.	Water. cc.	HCl. cc.	Alcohol. cc.	$BaCl_2$. gms.	Loss. gms.
14.	0.5011	3	25	15	0.4228	0.0043
15.	0.5096	2	25	10	0.4278	0.0066

The experiments of Series C were conducted in the same manner as those of Series A except that the amount of [illegible] indicated was added after the precipitation by hydrochloric acid.

The results show the alcohol neither decreased [illegible] amount of the solubility of the chloride.

Series D

Exp.	$BaCl_2 \cdot 2H_2O$ grams	HCl	Ba grams	[illegible]
16	[illegible]	[illegible]	[illegible]	[illegible]
17	[illegible]	[illegible]	[illegible]	[illegible]
18	[illegible]	[illegible]	[illegible]	[illegible]
19	[illegible]	[illegible]	[illegible]	[illegible]
20	[illegible]	[illegible]	[illegible]	[illegible]

In the experiments of Series D the weighed [illegible] was placed in an Erlenmeyer beaker and dissolved [illegible] cubic centimeters of water. The indicated [illegible] then added, and a stream of hydrochloric acid gas was passed [illegible] two hours into the cooled mixture. The precipitates were [illegible] treated as in the former experiments. The results show that [illegible] in the strongest possible solution at the ordinary temperature [illegible] hydrochloric acid, barium chloride is soluble to a [illegible] degree, this solubility amounting according to the first two experiments of the series to about [illegible] part in [illegible]. [illegible] to ten cubic centimeters of absolute ether were [illegible] tion before passing in the hydrochloric acid gas. The results showed that the ether seems to decrease the solubility of barium salt and therefore the experiments [illegible] were undertaken.

Series E

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

nient amount of hot water (about 2 cc.) and precipitation was brought about by adding the indicated amount of concentrated hydrochloric acid. The beaker containing the precipitate was then placed in cold water and the amount of ether shown in the tables was added and mixed with the solutions by thorough stirring. After standing for five or ten minutes the precipitate was filtered off and washed with concentrated hydrochloric acid containing about 10 % by volume of absolute ether and dried, sometimes in an air bath at 165°–175° C. and at others over a radiator giving a temperature of 175°–200° C. A constant weight was more quickly obtained by the latter method and it was used exclusively in the experiments of the subsequent series. In using it a low heat was used at first and the temperature was not increased until the precipitate was moderately dry. The results show that barium chlorid is practically insoluble in a mixture of hydrochloric acid and ether containing about one-sixth by volume of the latter. The average solubility calculated from the experiments given is one part in 122,000. The actual solubility is less than this since no account was taken of the volume of the washings which were at least equal to the original filtrates.

Series F.

Exp.	$BaCl_2 \cdot 2H_2O$. gms.	$CaCl_2$. gms.	HCl. cc.	Ether. cc.	$BaCl_2$. gms.	Loss. gms.
29.	0.5001	0.5	50	10	0.4250	0.0013
30.	0.4999	0.5	50	10	0.4250	0.0011
31.	0.5005	0.5	25	25	0.4260	0.0006
32.	0.5002	0.42	25	5	0.4258	0.0004
33.	0.5001	0.5	25	5	0.4255	0.0008
34.	0.5005	0.5	25	5	0.4251	0.0015
35.	0.5001	0.5	25	5	0.4254	0.0009
36.	0.5001	0.5	25	5	0.4258	0.0005
37.	0.5003	0.5	25	5	0.4261	0.0004
38.	0.1002	3.0	25	5	0.0842	0.0010
39.	0.0107	3.0	25	5	0.0080	0.0005
40.	0.5100	0.5	25		0.4328	0.0020

Series *F* was undertaken to test whether the mode of precipitating barium used in the preceding series would be of use in the separation of the barium from calcium. The experiments were conducted as in Series *E*, except that the calcium salt was dissolved with the barium chlorid. It was necessary to use more

water than in Series *E* to effect solution, but as the barium was uniformly the last to dissolve the effect was practically same as before. The results show that mixtures of barium calcium in all proportions are perfectly separated by this meth 0.0100 gm. of barium chlorid being separated with accuracy 3 gms. of calcium chlorid. The calcium does not show the sl est tendency to come down with the barium, and those experim in which separation was effected by the use of 25 cc. of hy chloric acid and 5 cc. of ether gave rather better results than t in which double this volume was employed. It is better no let the precipitations stand too long before filtration even if i cold, as the hydrochloric acid evaporates from the solutions experiments in which filtration was delayed for about two h e. g., Exps. 33, 34, 35, show a rather larger loss than the a age. That there is no advantage in increasing the amount of over the proportions used above is shown by Exp. 32, which comparable with Exp. 25. In the case of Exp. 4 in which ether was used the result is comparable with the experiments Series *A*. The precipitate was washed however with the m ture hydrochloric acid and ether.

Series

Exp.	Ba	HCl	MgCl₂	H₂O	HCl	Ether	Ca	Ba
	gm.	cc.	gm.	cc.	cc.	cc.	gm.	gm.
4	[illegible]	[illegible]	[illegible]	[illegible]	25	5	[illegible]	[illegible]
32	[illegible]	[illegible]	[illegible]	[illegible]	25	5	[illegible]	[illegible]
33	[illegible]	[illegible]	[illegible]	[illegible]	25	[illegible]	[illegible]	[illegible]
35	[illegible]	[illegible]	[illegible]	[illegible]	25	5	[illegible]	[illegible]

The experiments of Series *G* were made in exactly the same manner as those of Series *F*, except that varying amounts of magnesium chlorid were present instead of the calcium salt. The results are uniform and exact, and indicate that barium is separated from magnesium when the two are present in [illegible] tion. It is probable that the magnesium will be carried down in amount larger than is usual when it is present in the two treatments as under the same conditions it was found to be a [illegible] precipitate. The amount of magnesia [illegible] always found to be larger than the [illegible].

A [illegible] Barium chlorid is soluble to an extent [illegible]

ceeding one part in 20,000 in pure concentrated hydrochloric acid, but the solubility increases very rapidly with the diminution in the strength of the acid. In concentrated hydrochloric acid containing ether it is soluble to an amount not exceeding one part in about 120,000. To utilize this fact for the separation of barium from calcium and magnesium the chlorids of the earths are dissolved in the least possible amount of boiling water and precipitated by 25 cc. of concentrated hydrochloric acid with the addition of 5 cc. of absolute ether after cooling. The acid should be added drop by drop at first, allowing the precipitate formed to redissolve as long as possible, as the precipitate is thus obtained in a coarse crystalline condition and filters very quickly and is less liable to include foreign matter. After standing a few minutes the precipitate is to be filtered in a Gooch crucible, washed with hydrochloric acid containing about 10 per cent. of ether and dried at 150°–200° C. The method is accurate and rapid, and possesses the further advantage when a number of determinations are to be made that the precipitate may be dissolved off the felt by a little water and, after ignition, the crucible and felt may be used again without reweighing. A felt upon which half a dozen precipitates were weighed did not change its weight to the extent of one-tenth of a milligram. The fumes of the strong acid cause no inconvenience if the filtration is performed in front of a good flue. A gas flame may be used in the flue without danger from the ether which seems to be firmly held by the hydrochloric acid. A flame was used to increase the draught in all of the experiments given and with entire safety, even when the filtrate contained 50 per cent by volume of ether.

The author wishes in concluding to acknowledge his indebtedness to Prof. Gooch for many helpful suggestions freely given in the course of the investigation.

NOTES ON BUTTER.*

By Otto Hehner.

In the last number of *The Analyst*, reference is made to an observation which must have struck every analyst, namely, that

*The Analyst, June, 1892.

whilst, as a rule, genuine butters when carefully melted, yield a fat which is practically clear, margarines and badly adulterated samples melt very turbid.

I have for about a year past kept a record of most of the butter samples which have passed through my laboratory, and have noted the appearance on melting the samples in the water-oven, also the fact whether preservatives were found or not, together with the result of the analysis.

370 samples have thus been examined with the following results:

162 melted clear, and were genuine.
61 melted turbid, and were genuine.
81 melted turbid, and were adulterated.
66 melted clear, and were adulterated.

Of the 370 samples, 214 were preserved with borax or with boric acid, namely 119 genuine samples, or 53 per cent. of all genuine samples; and 95 adulterated ones, or 65 per cent. of all adulterated samples.

It is obvious from the above table, that while the majority of genuine samples, namely, 72.6 per cent. melted quite clear, and the majority, 55.1 per cent., of the margarines more or less turbid, nothing but the vaguest conclusions can be drawn from the appearance on melting. It is true, that in most cases in which the samples melted clear and yet were adulterated, the percentage of the admixture was comparatively small, say under 20 per cent. But I have met with adulterated samples containing 25, 30, 40, and even 94 per cent. of margarine, and yet they melted clear. These are isolated instances, but they remove the method quite out of the list of reliable ones.

I am not in a position to criticise the statements made by Drouot, Besana, and Wollny,* who all operated with a little apparatus devised by Drouot, whilst I simply melted my samples in a small beaker at the temperature of the water oven, but my results will be sufficient to make analysts cautious before placing reliance upon such a test.

The general use of boric preservatives should be noted.

*See abstract, Analyst, vol. 17, p. 100

NOTE ON THE LEFFMANN-BEAM METHOD OF DETERMINING FAT IN MILK.*

By Otto Hehner.

Drs. Leffmann and Beam have been kind enough to send me one of their centrifugal machines for the rapid estimation of fat in milk. I have made a few estimations of fat by means of this machine and give the results in the following table:

	Fat by Coil.	Fat by Centrifugal.
1	3.89	3.87
2	2.51	2.54
3	3.34	3.27
4	3.32	3.27
5	2.60	2.45
6	1.85	1.76
7	3.18	3.10

The results as far as it is possible to judge from so limited a number of determinations, are therefore quite as accurate as claimed for them by the authors of the process. I find one minute's whirling quite sufficient to separate the whole of the fat. It is therefore possible, by taking the specific gravity and the fat by the Leffmann-Beam process, to obtain an accurate milk analysis in a very few minutes, using Richmond's and my formula for the calculation of the total solids, or Richmond's slide rule.

I have not yet had time to investigate the exact *rationale* of the method, which is evidently not quite as simple as may at first appear. 15 cc. of milk are taken, 3 cc. of a mixture of equal parts of strong hydrochloric acid and of fusel oil are added, and then strong sulfuric acid up to the neck of the little bottle belonging to the machine. After careful mixing, so that all caseine has dissolved, hot dilute sulfuric acid is added up to the zero point of the graduation. Each division of the graduation corresponds to 0.15 cc. or to 0.1 per cent. by volume of fat. The figure thus obtained is to be multiplied by 0.86; this is, however, not the specific gravity of the butter fat, which when read off is but little above its melting point. I presume the figure is one accertained empirically, as the fat, after separation from the acid liquor beneath it, smells

*The Analyst, June, 1892.

strongly of fusel oil, and is evidently not pure milk fat, but a mixture.

DISCUSSION.

Mr. Alfred H. Allen thought that the graduation of the tubes was based on the fact that 0.86 was approximately the gravity of milk fat at 100° C., but with a substance with so high a coefficient of expansion as butter fat, even a moderate alteration in the temperature would, he thought, materially affect the volume registered. He would like to know whether Mr. Hehner had made the experiment with water instead of milk, and if so whether any fusel oil had risen to the top of the liquid.

The President replied that he had not tried the experiment.

Mr. Allen, continuing, said that it was difficult to follow the reasoning which led to the adoption of an arbitrary process. The inventor began by taking 15 cc. of milk; and then added a mixture of hydrochloric acid and fusel oil. He presumed the acid was used to obtain the fat in a kind of emulsion, and on then adding sulfuric acid the fusel oil was dissolved and the fat readily separated from the very dense liquid. It was also quite clear that any centrifugal apparatus would act better with two liquids of different densities, than if they possessed nearly the same density. The inventor could scarcely get very close or accurate results, unless he paid attention to the temperature at which he measured the fat, which could be very easily done by placing the tube in boiling water before observing the volume of the fat. The process described was an arbitrary process; but if it was really butter which came to the top, and not butter fat, *plus* fusel oil (which might be the case), it would be possible to confirm the result by the Werner-Schmidt process, and at the same time have a very useful preliminary indication of the amount of fat. In his opinion, the centrifugal plan ought to be capable of being very extensively applied for the sepation of liquids, and had, in fact, been recently applied to that purpose by Mr. Thorner.

Mr. H. Droop Richmond pointed out that if the factor 0.86 was probably obtained by dividing 0.89, the density of butter fat at about 50° or 60° by 1.032 the density of milk, the use of this factor would correct volume readings to weight percentages. He thought that the error caused by the contraction of the fat, owing to cool-

ing would be practically negligible and would fall within the unavoidable experimental error.

Mr. A. W. Stokes wished to ask whether the President had found that the fat rose by itself, because he (Mr. Stokes) had tried an experiment in a different sized glass, and he had found that casein rose from below and mixed with the fat, and results were difficult to read off. Could the fat be read off accurately?

Mr. Woosnam wished to ask if Mr. Hehner had tried leaving the acid upon the milk for any length of time, to see if it had then any effect upon the percentage of butter fat; or whether in order to get an accurate result, it was necessary to proceed at once with the "whirling" in the machine? Were there any black, solid particles left in the sulfuric acid mixture?

Mr. Hehner, in reply, said that he had not tried the experiment of leaving the acid in very long, because he had found from the few experiments made, that it was more satisfactory to perform the experiments at high temperature, and not to wait till the apparatus cooled down. In reply to the question asked by Mr. Stokes, he stated that if the experiment were properly done, there was absolutely no emulsion between the acid and the fat.

ON THE PROPORTION OF WATER IN BUTTER.*

By Alfred H. Allen.

A good deal of interest is attached at present to the proportion of water which may be properly contained in butter, in consequence of the sudden appearance in the market of butters containing an unusually large percentage of water. In the years 1877 and 1878, the West Riding officials submitted to me several samples of butter which were found on analysis to contain large proportions of water. Thus I certified to 19.83, 22.24, and 25 per cent. respectively. Action was taken on my certificates and convictions obtained. Since that time and quite recently, of the thousands of samples of butter which have passed through my hands, hardly any have contained a marked excess of water. It would scarcely have escaped notice in the ordinary process of preparing the butter-fat, and, in fact, the recent cases have forced themselves on my attention during the ordinary process of analysis, there being no

*The Analyst, June, 1892.

previous suspicion that an abnormal proportion of water was present.

The first case among those of recent occurrence was that of a sample, said by the defense to be Cork butter, churned by small farmers from the produce of one or more cows each. On analysis, I certified it to contain 22 per cent. of water, the amount actually found being 22.44 per cent., and added that "In my opinion any proportion of water in excess of 16 per cent. as a maximum should be regarded as an adulteration." Without any evidence being adduced for the defense, it was submitted to Somerest House, when Messrs. Bell, Bannister and Lewin reported that "the sample of butter referred to in the annexed letter was received here on the 9th inst. (December), securely sealed. We have analyzed the butter and declare that it contains 22.98 per cent. of water. We are of opinion that such proportion of water is in excess to the extent, of at least 5 per cent." This certificate is eminently characteristic. It states the minimum adulteration without going further and saying what was the excess of water above the average proportion in butter. It is evident, also, that it fixes the Somerest House limit for water in butter at 18 per cent., and affords one more illustration of the perverse custom of the Somerest House Chemists of straining every point in favor of the defense, instead of occupying the more consistent position of impartial referees of the Court.

On page 64, *et seq.*, of his work on "Food," vol. ii., Dr. James Bell gives results of the analysis of 113 samples of butter, which he says were selected so as to obtain, as far as possible, fair representative samples of butter produced under different conditions; and in the *Report of the Board of Inland Revenue*, 1876, he states that "the samples may be taken as fairly representing the various qualities of butter as made and brought to market by farmers both in England and Ireland. Every care was exercised by the Board's local officers in procuring them, and there can be no question whatever as to their being genuine." I am afraid people who live in the rough world, outside the circle of Arcadian simplicity in which Dr. Bell apparently dwells, will be inclined to think that the Irish peasant-farmer is quite capable of taking, and even likely to take, a wicked delight in supplying an exciseman with an abnormal article. Dr. Bell's remarkable conclusion further presumes

that no farmer introduces an excess of water into butter, or makes an addition of foreign fat. This assumption is strictly opposed to my own personal knowledge that margarine is, and has for years past, been habitually bought by dairy-farmers for incorporation in the butter subsequently made and brought to market. He further contends that butter not made for sale must necessarily be genuine, and so practically extends the definition of "genuine" to any butter which has passed through the hands of a careless or incompetent dairymaid, who thereby becomes the arbiter of quality. But Dr. Bell's more recent opinion, as laid down in his work on "Food," vol. ii., page 47, is that "*a greater amount of water in butter than 12 per cent. is unnecessary, so far as attaining a good appearance is concerned, and anything over 16 per cent. is injurious to the keeping qualities of the butter.*" Clearly, it was Dr. Bell's opinion at the time he published his second volume that 16 per cent. is the maximum limit of water to be allowed in butter, in which opinion I cordially concur, but in the modification of his opinion for the guidance of local magistrates, who expect to receive from him impartial advice, he fixes the limit at 18 per cent., and omits all mention of either the average or maximum proportion in well-made butter. This deplorable omission, which is consistent with the usual practice of the Somerset House Chemists, is of course, directly conducive to adulteration.

In the Article on "Butter" contributed by Dr. Bell to Thorpe's *Dictionary of Applied Chemistry* (vol. ii., page 300), it is stated that "in commercial butters the water has been found to vary from 4 to about 18 per cent." Here, therefore, Dr. Bell abandons his position that the exceptional butters included in his 113 commercial samples were "genuine" and again fixes his maximum for water at "about 18 per cent.," which may therefore be regarded as the present Somerset House limit.

There has lately been an organized and systematic attempt, emanating from certain German ports, to place heavily-watered butter on the English market, and hence public analysts should be on the look out for samples of butter so sophisticated.

In my more recent certificates on watered butter, I have actually quoted Dr. Bell's words, giving him as an authority for the statement that "a greater amount of water than 12 per cent. is unnec-

essary, and anything over 16 per cent. injurious to the keeping qualities of the butter," and have stated my agreement with that opinion. Such a definite course as this is desirable in the face of the one-sided certificates issued by Somerset House, and of the fact that the solicitor for a defense in a recent case actually contended that *any* amount of water in butter was allowable, seeing that the Legislature had not defined the amount, "finding it impracticable to do so." Such assertions as these are usually made in the absence of the analyst, and if he becomes aware of them, it is only by accident and when the case is at an end; but it behooves public analysts to correct such flagrant misstatements of the scope and purpose of the Sale of Food and Drugs Act.

In 1875, the Society of Public Analysts proposed and adopted for butter the limit of 80 per cent. for butter-fat, leaving 20 per cent. for salt, curd and water. I think this is a perfectly proper limit, but it may be worth while to restate the fact, as I notice that at a recent convention of the American Association of Agricultural Chemists, the Society's limit was erroneously stated to be 85 per cent.*

In several cases since the one referred to Somerest House, I have met with upwards of 20 per cent. of water in butter, and proceedings have been taken and convictions obtained on my certificates. In one instance the proportion of water reached 29 per cent!

In proceedings recently taken on my certificate for the sale of butter containing 21½ per cent. of water, two inspectors from Cork Butter Market were witnesses for the defense. Their evidence was of so startling and novel a character that a short reference to it will not be out of place. They swore that they examined a very large number of samples daily; such a number that the testing of each must have been completed, if I remember their figures rightly, in a fraction of a minute. They observed the taste, smell, color and consistency of the butter, and were inclined to dispute the analysis, on the ground that butter with so large a proportion of water would not have escaped their attention. They stated that the proportion of water met with in Irish butter sometimes reached 20 per cent; but it did not appear that they had ever actually as-

*To my astonishment, I find that the S. P. A. limit is incorrectly stated at 85 per cent., in vol ii. of my "Commercial Organic Analysis."—A. H. A

certained the quantity or deputed an analyst to do it for them. They, however, swore that any abnormal proportion of water in the sample was probably due to the weather; for in wet weather the food of the cows was of course wetter, and hence the butter contained more water! This novel and highly interesting statement was made in the witness box. Further, they discriminated between "water in solution" and "water in suspension," but which of these curious forms was the normal, and which the abnormal constituent of the butter, was not made clear.

I find the proportion of water in butter to be most conveniently determined by placing 5 gms. of the sample in a small tared beaker, and exposing it in an air-bath, to a temperature not exceeding 110° C., until no more globules of water can be observed on looking at the beaker from below. Generally, the water can be completely expelled in about one hour. The curd and salt can be subsequently determined in the same quantity. After evaporating the water, the fat is re-melted, and filtered into a small beaker kept in the water-oven. The residual matter is rinsed on to the filter with re-distilled petroleum spirit, and washed with petroleum spirit until free from fat. The filter is then dried at 100° C., and the contents scraped off and weighed. After weighing, the residue, which represents the curd and salt of the butter, may be examined under the microscope for starch, cellular tissue, &c., and then, if desired, treated with cold water, and the solution further examined or titrated with standard silver solution to estimate the salt. Usually, however, it is sufficient to ignite the residue in porcelain at a low temperature, and regard the non-volatile matter as salt, the combustible as curd.

Some butters are far from being homogeneous, and when possible it is preferable to work on 25 or 50 gms. rather than on smaller quantities.

DISCUSSION.

The President remarked that lately, with the close competition in the butter trade, when 5 per cent. of margarine added to butter made mixing a profitable business, the attention of butter mixers had again been directed to the addition of water. As Mr. Allen had said, having regard to the systematic manner in which butter

containing water was forced upon the market by unscrupulous dealers, every per cent which such men could get [illegible] the referees at Somerset House would be a considerable gain to them and loss to the public. In his opinion there was no [illegible] why a butter should contain more than [illegible] per cent [illegible]. When the percentage of water rose above [illegible] it was [illegible] added or negligently left in, and the excess was [illegible] mental to the public but to the butter merchants themselves. He had been told by a merchant that, out of [illegible] particular farmer, out of every hundredweight of butter he lost three to four pounds in transit. On analyzing [illegible] butter referred to, it was found to contain [illegible] Irish Inspectors would call [illegible] undissolved water.

Mr. Cassal asked what method Mr. Allen used [illegible] water in butter? He wished to ask whether [illegible] samples of butter the existence of any substantial [illegible] water was rendered evident? He understood Mr. Allen [illegible] this was so, and it so [illegible] agreed with his own experience.

Mr. Stokes stated that he examined every sample [illegible] received microscopically, and his experience was [illegible] contained an abnormal [illegible] of water [illegible].

Some years ago it was [illegible] times of water in butter [illegible] so frequent. Under the [illegible] a sample contained more [illegible] with the [illegible] mal amount of water.

Mr. Cassal [illegible] Mr. Stokes [illegible] on the microscopic [illegible] purpose of showing [illegible].

Mr. Stokes [illegible].

Mr. [illegible] Mr. S[illegible] [illegible]

Mr. Stokes expressed his readiness to read a paper before the Society on the subject.

Mr. Allen asked Mr. Stokes if he would at once explain to the Society the way in which he manipulated with the microscope in order to effect this desideratum.

Mr. Stokes replied that he took a butter, just as it came to him, and scraped a large surface clear. He then took a thin layer below this, and placed it on an ordinary microscope slide; over that he placed a microscopic cover-glass, and pressed this down, so that the butter formed a thin wedge. He now crossed the polarizing prisms so that the field of view was absolutely dark. On placing the slide between the prisms, if there was a trace of butterine or margarine, say within 10 per cent., at once a glimpse of light came through. Badly constructed polariscopes let light pass without interposing an object, and are useless for this purpose. In case of a genuine butter, there was no illumination at all. He had never once found this system fail. No selenite plate should be used, since its results are often delusive.

Mr. Allen replying generally to the remarks made, said that the test mentioned by Mr. Stokes had quite recently appeard in a trade journal, the only variation being that in that paper a plate of selenite was recommended, which he did not gather was the case with the method described by Mr. Stokes. Since that event, he had been asked by butter merchants if he was acquainted with the test. He had replied that he did know it, but that, in his opinion, it was only of value where large proportions of margarine were in question. In a paper recently published in America, it was proposed to dissolve the butter in a drop of oil, and examine it. Since the appearance of the article he had just referred to, he had tried the experiment, and he had found marked double refraction in genuine butters; and in the case of samples, which he believed to contain margarine in some cases he found double refraction, and in others, none. This caused him to come to the conclusion that there was more to be learnt before the process could be relied on.

He would like to indorse what the President had said with regard to the undesirability of giving analytical data in the case of butter analyses. He contended that their clients had absolutely no right to demand the figures on which they based their opinion

as to the presence or absence of margarine; and he had, therefore, declined in recent instances to give them. He was told a few days before the meeting that a letter written by a German house, contained the statement that "Mr. Allen was entirely behind the age; that he should use the Reichert test, and he would arrive at the same results as other gentlemen." Seeing that he (Mr. Allen) had been among the first to adopt the Reichert distillation process, and recommended it to his brother chemists (ANALYST, x., 103; xii., 11; xiv., 5), and that at a period when the President (Mr. Hehner), doubted its value, even as a sorting test, this allegation was somewhat wide of the mark. But he held very strongly that an opinion on butter should not be based on the result of any single test. There were butters now in the market which were very skilfully adulterated, and it was only by the combined application of several tests that the fraud could be discovered; in fact, to his knowledge, it had escaped recognition in several instances of late. Analysts ought to be very careful not to give to their natural enemies, the adulterators, information respecting the methods they employed for the making of analyses. The discussions at the meetings of the Society were extremely valuable; but when it was known that THE ANALYST was bought reguarly by all sorts of people, in order to see what could be done by analysts, and what could not be done, it was evidently extremely undesirable to let the general public know everything they were doing.

Mr. Cassal drew attention to the fact that a note had appeared in the *Times* on the adulteration of Normandy butter; and that it was pointed out therein that science failed entirely to detect certain percentages of margarine in butter, but that a test had now been devised, which was all that could be desired, and which "could be applied by an 'inspector' with the aid of a boy." He received Mr. Stokes' statement with all respect, and he would look forward with pleasure to the further information he had promised to lay before the Society. He, nevertheless, entertained considerable doubt as to the propriety of applying microscopic examination as the sole test for the passing of samples of butter.

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THE DETERMINATION OF CARBON DIOXID IN THE AIR OF BUILDINGS.

BY AUGUSTUS H. GILL, PH.D.

In the only treatise upon air analysis in the English language, the method given for the determination of carbon dioxid admits of no great accuracy, as results varying 6 per cent. from an average, and 10 per cent. among themselves, would indicate. The writer recommends the following method, which has been in use in the laboratory in almost the present form for fifteen years.

Both methods are those of Pettenkofer,* which consists in bringing a large known volume of air in contact with standard barium hydrate.

The bottles used for containing the samples are ordinary green glass gallon or two gallon bottles, holding 4400 or 8800 cc. respectively; they are calibrated with water, by weighing upon scales sensitive to 5 gms., and their capacity marked upon them with a diamond. They may be conveniently transported from place to place in a partitioned basket made for the purpose.

The bellows there suggested (wooden disks joined by a strip of rubber, with no valves) was found troublesome to manipulate, and has given way to one about to be described. The nozzle of an ordinary 9 inch blacksmith bellows is removed and the opening fitted with a valve opening outward; this is made by tying a bit of chamois skin over a cork which fits over a tube passing into the nozzle opening. By varying the position of the cork, different degrees of tightness of valve are attained. To the other opening of the bellows, closed with its usual valve, is fitted a cork carrying a four-foot piece of 5/8 inch rubber tubing terminating in a light

*Annalen. 2. Supp. Band. p. 1.

two-foot brass tube, bent for insertion into the bottles. Instead of the bellows, a small 6 inch fan blower, the driving parts of which are connected by rubber bands to render it noiseless, can be used if it is desired to decrease the bulk of the apparatus.

The bottle is fitted with a rubber stopper, carrying a glass tube, closed by a small unperforated rubber nipple; both the stopper and nipple have been digested with caustic potash and thoroughly washed to remove the superficial zinc oxid.

The air to be tested is drawn into the bottle by means of the bellows, fifteen strokes being taken, sufficing to fill a four liter bottle four times, thus insuring a representative sample. In collecting this sample the atmosphere in the room should be as quiet as possible; care must be exercised to avoid the drafts or the proximity of people.

When used the bottles should be *clean* and *dry*; by clean is understood containing nothing to affect the barium hydrate used. When wet the standard barium hydrate is diluted, and as the whole of it is not used, the determination is lost, unless the amount of water present be accurately known.

The operation of drying the bottles is by no means as troublesome as it would appear. A small closet heated by steam and provided with suction, enabling a current of hot air to be drawn into the bottles, suffices to dry a dozen bottles in half an hour. The samples are brought into the laboratory, the temperature of which should be a little higher than that of the place where they were taken, and allowed to stand half an hour, or until they have attained its temperature.

50 cc. of the standard barium hydrate are now run in rapidly from a burette (the tip passing entirely through the tube in the stopper), the nipple replaced, and the solution spread completely over the sides of the bottle while waiting three minutes for the draining of the burette, before reading, unless it be graduated to deliver 50 cc. The bottle is now placed upon its side, and shaken at intervals for 40–60 minutes, taking care that the whole surface of the bottle is moistened with the solution each time. The time of absorption, ten minutes, recommended in the treatise, is much too short, as the disappearance of the last traces of carbon dioxid is very slow indeed, half an hour in many cases being insufficient.

At the time at which the barium hydrate is added, the temperature and pressure should be noted. At the end of the above period, shake well to insure homogeneity of the solution, remove the cap from the tube, and invert the large bottle quickly over a 50 cc. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, withdraw a portion of 15 or 25 cc. with a narrow stemmed spherical bulbed pipette and titrate with sulfuric acid* (1 cc. equals 1 mgm. CO_2) using rosolic acid as an indicator. The difference between the number of cubic centimeters of standard acid required to neutralize the amount of barium hydrate (*e.g.*, 50 cc.) before and after absorption, gives the number of milligrams of carbon dioxid present in the bottle.

This is expressed in cubic centimeters under standard conditions, and divided by the capacity of the bottle under standard conditions, and the results reported in parts per 10,000. To reduce the air in the bottle to standard conditions, a hygrometric measurement of the air in the room from which the sample was taken, is necessary. This in ordinary cases is usually omitted, as the object of the investigation is *comparative* results, as regards the efficiency of ventilation, and the rooms in the same building would not vary appreciably in the amount of moisture in the atmosphere. This correction may make a difference of about 0.15 parts per 10,000.

Some of the results obtained by our students by the preceding method are as follows:

Expressed in parts of CO_2 per 10,000.

Room No. 24.	No. 43.	No. 37.	No. 34.	No. 34.	No. 23.	Outside Air.
5.54	7.34	4.94	5.16	5.53	4.54	3.13
5.59	7.27	4.89	5.12	5.52	4.46	3.09

The subjoined results are interesting as showing rate of vitiation of the air in a well-ventilated lecture room. It is 15 feet high, having a capacity of 24,000 cubic feet, and supplied with 185,000 feet of air per hour, from three flues; 225 students were present.

*Sulfuric acid, in distinction to oxalic acid, enables one to estimate the excess of barium hydrate in presence of the suspended barium carbonate, and also of caustic alkali, which is a frequent impurity of commercial barium hydrate. Professor Johnson, in the American edition of *Fresenius' Quantitative Analysis*, calls attention to the fact that the normal alkaline oxalates decompose the alkaline earth carbonates, so that the reaction continues alkaline if the least trace of soda or potash be present. The sulfuric acid may be prepared by diluting 46.51 cc. normal sulfuric acid to a liter.

	Time	1st Day [illegible]	2nd Day [illegible]
Before lecture	11 35	[illegible]	[illegible]
	12 10	[illegible]	[illegible]
	12 20	[illegible]	[illegible]
	12 30	[illegible]	[illegible]
	12 40	[illegible]	[illegible]
	12 50	[illegible]	[illegible]
End of lecture	1 00	[illegible]	[illegible]
	1 30	[illegible]	[illegible]

The following shows the distribution of carbon dioxide in an ordinary theater

	[illegible]
Floor	[illegible]
1st Balcony	[illegible]
2nd Balcony	[illegible]
Gallery	[illegible]

Laboratory of Sanitary Chemistry and Gas Analysis
Mass. Institute of Technology, Boston, Mass.

IMPURITY IN ZINC

By Frank [illegible]

In the estimation of phosphorus by the reduction of the molybdic acid of the phosphomolybdate precipitate by means of zinc and sulfuric acid, and subsequent titration with standard potassium permanganate it becomes necessary to have a precise knowledge of the oxidizable matter contained in a solution of an approximate weight of zinc.

To dissolve zinc in dilute sulfuric acid is a tedious and [illegible] possible operation.

The addition of even small quantities of [illegible] the amount of oxidizable matter is small as it [illegible] seems of no [illegible].

To avoid this [illegible] the same time [illegible] the following [illegible] adopted in this laboratory.

A [illegible] solution was [illegible] and the [illegible] were [illegible] Experiments showed that [illegible] were [illegible] potassium permanganate [illegible] phosphorus. Next [illegible] with the exclusion [illegible] H_2SO_4, 1.84 sp. gr. [illegible] H_2O [illegible]

and the volume made up to 500 cc. with cold, boiled water, and titrated with the above potassium permanganate solution.

Four samples of the same twenty pound lot of zinc required 32.8 cc., 32.7½ cc., 32.7½ cc., and 32.8 cc., showing that the 5 gms. of zinc required on an average 0.275 cc. potassium permanganate solution, or since about 10 gms. is consumed per determination of phosphorus, $2 \times 0.275 = 0.550$ cc. should be subtracted from the reading of the burette before the per cent. phosphorus is calculated, and we see with a solution of above strength

$$\frac{0.550 \times 0.0001}{5} = \frac{0.000055}{5} = 0.0011 \text{ per cent.}$$

that where 5 gms. of sample is operated upon the percentage of phosphorus would be too high by 0.0011 per cent. were this correction not made. Other specimens of zinc have been treated with equal success in obtaining the correction. The same *modus operandi* may serve to find the iron correction, and it would seem that by carefully oxidizing 0.2 gm. wire in solution in sulfuric acid and passing through the Jones' Reductor that the increase in amount of potassium permanganate solution required, above that required in another 0.2 gm. portion dissolved in the ferrous condition would yield a valuable correction for the reductor, especially when care is used to preserve about the same amount of free acid in all samples passing the reductor.

The following are some results by Dr. Drown's method, using this correction, compared with the magnesia method :

	Magnesia.	Drown.
Common Muck Bar	.274 per cent.	.272 per cent.
" " "	.112 "	.114 "
Bessemer Iron	.045 "	.046 "
" "	.105 "	.106 "
Billet	.088 "	.088 "
Special Muck Bar	.018 "	.019 "
" " "	.012 "	.011 "
" " "	.008 "	.006 "
" " "	.010 "	.012 "
		Volumetrically with Zn.
Chandler Ore with Residue	.044 "	.043 "
Angeline Hard	.011 "	.012 "

LABORATORY OF
STEWART IRON COMPANY, LIMITED.
SHARON, PA., July 25, 1892.

THE ANALYSIS OF ARTIFICIAL COLORING MATTERS.

By Louis Joseph Matos, M.E.

It is proposed to detail in the present paper the methods followed in the laboratory of a large textile establishment, for the examination of the artificial coloring matters. As is well known, very large quantities of these colors are imported into the United States, and eventually find their way, through sales agents or otherwise, to the consumers, very few of the latter buying directly from the manufacturer. These colors are produced at the manufactory, ordinarily in crystalline form, some, however, being obtained in crusts or cakes, and others still, in the form of flocculent precipitates; except in very few instances are the products put upon the market in the condition that they are obtained at the works. They are mostly ground to a fine powder and mixed with varying quantities of inert subtances, such as anhydrous sulfate of soda, sulfate of magnesia, chlorid of sodium ; in some cases, carbonates, starches of various kinds, flour, dextrin, etc., The thought must not be entertained that these subtances are adulterants in the ordinary sense; they are added for the purpose of *diluting* the intense color which the factory product possesses, for if such was not done, it would be very difficult for a dyer to judge the amount of dye he requires to produce a certain desired effect. Different coal-tar colors require different amounts of diluents; some are mixed with twenty-five, or fifty per cent., and in several instances the commercial dye contains only ten per cent. of real coloring matter. Starches, in the dilution of this class of colors, play, also a secondary part; it is well known that many of the tar coloring matters, notably, some of the alkali salts, are extremely deliquescent, and to them is added the starch, which acts as an absorbent of moisture, and tends to keep the dye dry and in a powder, acting in the same manner as when it is added to a baking-powder, prevents caking. When these substances are added in definite proportions, and for the above purposes, they cannot be looked upon as true adulterants, and when their percentage does not sensibly vary in succeeding lots of dye purchased, they ought to be passed. True adulterants have been met with in the form of sand, iron-filings, plaster, etc., but only in rare cases.

The chemist of a textile establishment ought to be independent of the dyer, in so far as relates to the application of colors upon fabrics, but he should be thoroughly familiar with the general methods of dyeing, and what is very important, the compatibility of colors. In many cases the dyer uses his own judgment in the mixing of individual colors, with the result that the goods are streaky, spotted, etc., and rather than acknowledge that the fault is due to his lack of knowledge of the properties of the dyes used, condemns the colors off-hand, or tries again with another set. The young textile chemist cannot spend too much time in determining by actual laboratory work, upon small quantities of material and fabric, and under varying conditions, the compatibility of colors, and also the general capabilities of each color.

The laboratory is provided with a large number of four ounce bottles for "check samples," and when new lots of dyes come in, the cans are opened, and about three or four ounces of substance are removed from each, carefully but rapidly mixed, and the sample bottle filled. This furnishes an average sample, and is labeled:

Name of Dye .....

Received from .....

Date ..... *Lab. No.* .....

Remark .....

Determination of Moisture.—For this, one to three gms. of the dye are weighed out in a tared porcelain dish, about two inches in diameter, and heated at a temperature of 100° C. to 105° C. in an air bath; the air bath is made of heavy copper, with a double bottom, and is large enough to accommodate from twelve to eighteen dishes. The dishes are allowed to cool and weighed, heated and weighed again, or until the weight is constant. The loss is reported as moisture. During the drying it is often convenient to place over the dishes circular pieces of plain white paper, and note from time to time the volatility of the color.

Insoluble Matter.—The contents of the dish from the moisture determination are taken and dissolved in a little hot water, transferred to a convenient-sized beaker, diluted with water, allowed to stand for a while, decanted through a *small* tared filter, finally bringing the sediment on, and washing until no color remains. Dry as usual and weigh. In dissolving the dye for this determination note particularly any odor of dextrin, which will be apparent if that substance is present.

Chlorid of Sodium.—As many coal-tar colors contain chlorin in combination, the direct addition of nitrate of silver is inadmissible. For the determination of salt, an indirect method gives very good results. A weighed quantity of the dye (about two grams) is ignited in a capacious porcelain crucible, the ash heated with boiling water, filtered from insoluble matter, nitric acid added, and the precipitation proceeded with in the usual manner. The use of a large crucible for the ignition is necessary from the fact that a large number of the tar colors swell up to many times the original volume upon the application of heat. The precipitate is filtered, washed, dried, etc., and from the chlorin found, the amount of salt is calculated. In some cases, the writer has obtained good results with the following method: A known weight of the dye is dissolved in water, sulfuric acid added, and all the color removed from the solution by the repeated agitation with ether in a separatory funnel. The chlorin is precipitated in the usual manner from the colorless aqueous solution remaining.

Sulfate of Soda.—This is always determined from the amount of barium sulfate obtained by ordinary precipitation from a hydrochloric acid solution. In the event of the dye being a sulfonated product, it is necessary to precipitate with barium chlorid in hot solution, in which case barium sulfate and barium sulfonate are thrown down together, filter, wash well with water, and while on the filter, treat with a solution of ammonium carbonate. This converts the barium sulfonate to carbonate, and is easily removed by the addition of dilute hydrochloric acid. The residue, if any, will be the sulfate. Wash, dry and ignite.

Sulfate of Magnesia.—Whenever magnesia is found in a dye, upon qualitative examination, adulteration is assured in the sense previously mentioned, because magnesia is never a chemical constituent of tar colors. It is estimated by direct determination

in the ash, by dissolving in dilute hydrochloric acid, filtering, and to the filtrate adding ammonium chlorid and hydroxid to perceptible odor, followed with sodium ammonium phosphate, and allowing to stand. The precipitate is weighed as magnesium pyrophosphate ($Mg_2P_2O_7$).

Dye-stuffs containing sulfate of magnesia do not mix well with some dyes which are used for printing goods to be subjected to the steaming process for fixing colors.

Carbonates.—The safest way to determine these substances is to use a carbonic acid apparatus. The form the writer has always found most convenient is Dr. Wetherill's ; whatever form is used, it should be light in weight.

Dextrin.—If its presence is betrayed as previously mentioned, weigh out two to four gms. of the dye in a small tared beaker with a short rod, dissolve in a small volume of water, and add a small quantity of absolute alcohol, when the dextrin will be precipitated and tenaceously adhere to side of the beaker and rod, allow to stand awhile, pour out carefully, wash with alcohol several times, dry and weigh. Any insoluble matter present will be enclosed with the precipitated dextrin ; the weight of the insoluble matter found in the first instance, must be subtracted from the combined weight in this case, to obtain the true weight of the dextrin.

Starch.—This substance is insoluble, and by weighing a quantity of the dye, dissolving in water, starch will remain with other insoluble matter, by filtering, washing, drying and weighing, the total insoluble matter is obtained, and by igniting this dried residue, and weighing, the combustible part can be reported as starch or flour, of course, based upon a microscopic examination of the sediment obtained by allowing some of the dissolved dye to stand in a conical test-glass. Recourse should always be had to the use of the solution of iodin, and iodid of potassium when testing, microscopically, for starch.

Sugar.—Sugar is occassionally met with in crystalline dyes only. It can be estimated in the same manner as for dextrin, with fair results when rapidity is desired, or accurately, by precipitating the coloring matter from a weighed quantity of dye, with basic lead acetate, and polarizing, or by inversion and titration with Fehling's solution.

COMPARISON OF METHODS FOR THE STANDARDIZATION OF ACID AND ALKALINE SOLUTIONS.

By Charles L. Parsons.

Owing to the recent interest in methods for the accurate determination of the strength of alkalimetric and acidimetric solutions, made manifest by numerous published papers and discussions, and to the undoubted importance of the subject, I have made many analyses by the more important methods in order to compare results.

Three solutions were prepared; one of hydrochloric acid about fifth normal, and one each of ammonia and barium hydroxid of approximately tenth normal strength. These are the solutions commonly used in this country. They were made from pure chemicals and were protected from addition of moisture and of carbon dioxid where necessary.

The ammonia and barium hydroxid solutions were purposely made so that two cubic centimeters of either should exactly equal one of the hydrochloric acid.

The strength of the ammonia was determined directly by means of ammonium platinic chlorid, by potassium tetroxalate, and by acid potassium tartrate. Portions of the barium hydroxid solution were precipitated as barium sulfate or were titrated against potassium tetroxalate. The strength of the hydrochloric acid was ascertained; by titration against ammonia distilled from a known amount of ammonium chlorid; by pure, transparent and colorless Iceland spar; and by precipitation as silver chlorid.

The remainder of the results given are, of course, obtained by comparison of the solutions, but are none the less important and accurate. Lack of time and, for the time being, inefficient batteries prevented my working with the copper sulfate method of Hart & Croasdale,* and I realize this to be a serious omission, which circumstances rendered unavoidable.

The indicators used were for each case those which in my experience have proven to be the best.

The following are the results obtained:

*J. Anal. Appl. Chem, 4, 424.

Standardization of HCl, NH_3 and $Ba(OH_2)$ Solutions by Different Reagents.

1 cc. HCl solution = 2 cc. NH_3 solution.
1 cc. HCl solution = 2 cc. $Ba(OH)_2$ solution.

METHOD.	Indicator.	Gms. NH_3 in 1 cc. solution.	Gms. HCl in 1 cc. solution.	Gms. $Ba(OH)_2$ in 1 cc. solution.
By precipitation as $(NH_4)_2PtCl_6$		.001545	.006634	
By neutralization with $HKC_2O_4H_2C_2O_4 + 2H_2O$	Litmus	.001560	.006698	
By neutralization with $KHC_4H_4O_6$	Litmus	.001564	.006716	
By precipitation as AgCl		.001558	.006679	.007822
By pure pulverized Iceland Spar	Cochineal	.001567	.006728	.007880
By distillation of NH_3 from NH_4Cl	Cochineal	.001563	.006717	.007866
By precipitation as $BaSO_4$			.006676	.007820
By $HKC_2O_4H_2C_2O_4 + 2H_2O$	Phenol-phthaleïn		.006722	.007875

The potassium tetroxalate was prepared by myself from K_2CO_3 and $H_2C_2O_4$ and was recrystallized six times, being washed once with distilled water by decantation after each crystallization.

The acid potassium tartrate was prepared by myself from the purest cream of tartar obtainable, was heated with HCl, washed and crystallized according to directions of Dr. Bornträger (*Ztschr. anal. Chem.* **31**, 56), and was further recrystallized three times, as the directions given did not prove sufficient in my hands to give a pure salt.*

A glance at the above table indicates one general feature, which is, that in every case the figures obtained by gravimetric methods are lower than those obtained by the volumetric. This is probably what would be generally expected; for, of the two, the tendency toward loss of substance and consequently lower results is certainly more for methods involving the manipulation incident to gravimetric ones. The results are, however, on the whole good. Those obtained by silver chlorid and barium sulfate agree closely, and the lower result obtained by ammonium platinic chlorid is easily accounted for by the comparatively high solubility of the salt. I

*See second article following.

have no hesitancy, when convenience is also taken into consideration, in placing the determination as silver chlorid at the head of gravimetric methods.

With volumetric methods the case is somewhat different. The absolute composition and purity of the salt used as a standard and its efflorescent and deliquescent properties become of the greatest importance. No substance whose accurate composition cannot be definitely known at any time can be used. I will take up each method by itself.

By distillation of ammonia from an alkaline solution of ammonium chlorid results seem to be invariably high while still agreeing fairly well with other methods. This is the general testimony of chemists, and the reason may probably be ascribed to impurities in the so called chemically pure salt. Higher results still are obtained after all precautions are taken. The reaction obtained with cochineal is of course sharp, and duplicates generally agree closely.

The Iceland spar used was transparent and colorless, was finely pulverized, and dried for several hours at 100°. The results here are also slightly high, but the tendency is also toward high results, not only on account of the danger of the presence of minute quantities of carbon dioxid, not removed by boiling, but from the fact that the titration is carried from acid to alkaline reaction and calculations made directly on acid. The one or two extra drops of alkali required to show alkaline over acid color easily account for most of the increase. Unless the mineral is very finely pulverized, it dissolves but slowly in the very weak acid.

The results obtained by acid potassium tartrate were near the average after the salt was obtained pure. The preparation of the salt is, however, tedious on account of its extreme insolubility, and the tendency is to be too acid, and consequently to give low results.* The chief difficulty encountered, however, was my inability to find an indicator except phenol-phthaleïn, whose reaction should be as definite as desired in its presence. It was found necessary for accurate work to average several analyses. Four or five drops of decinormal ammonia solution were generally necessary to show certain color in either direction. The salt does not con-

*See second article following.

ain water of crystallization, and may be dried at the temperature of boiling water.

The determinations made by the aid of potassium tetroxalate are almost exactly the average of all results, both gravimetric and volumetric, and are, in my opinion, the most accurate. I shall attempt to show in the following paper that the salt is easily and definitely prepared, and that the chief objection raised against it, viz., that it contains water of crystallization, is in this case, at least, inoperative. Its reaction with litmus is decidedly sharp for an organic salt, and most excellent duplicates are easily and quickly obtained. The fact that much of the tetroxalate on the market is a mixture of the tetra and normal oxalate, and that before recrystallization many have not first added excess of oxalic acid does, to my mind, account for the recent disrepute in which the salt has apparently fallen.

POTASSIUM TETROXALATE.

By Charles L. Parsons.

The following set of analyses was undertaken to find out, if possible, the reason why potassium tetroxalate has failed to give good results in the hands of many chemists as a standard for alkalimetric work while it has been held by others to give perfect satisfaction.

In order to study commercial samples, an order was sent to six different firms for one ounce of their *best* tetroxalate and part of the firms were asked to send one ounce of each make they had in stock, giving manufacturers' names. The results on the samples received with a few samples from other sources are given in the following table:

Potassium Tetroxalate.

Comparison of different makes, keeping qualities, hygroscopicity recrystallization, etc.

Litmus, prepared according to Sutton, having been found to be the best indicator, was used.

1 cc. NH_3 solution = .001558 by comparison with HCl by AgCl.

No.	From Whom Received.	Manufacturer or Name on Label.	How Prepared for Analysis.	Amount of NH_3 in 1 cc. NH_3 solution.
1a	Mr. Van Slyke*	Baker & Adamson	As received.	.001731
b	Mr. Van Slyke	Baker & Adamson	Recrystallized 3 times. Dried over H_2SO_4.	.001569†
2a	Eimer & Amend	Eimer & Amend	Recrystallized 3 times in September, 1889, with excess of oxalic acid. Not dried for 2 years 8 months.	.001574‡
2b	Eimer & Amend	Eimer & Amend	Same, but dried 18 hours over H_2SO_4.	.001575
3a		Made in our Laboratory from K_2CO_3 and $H_2C_2O_4$.	Recrystallized 3 times. Dried over H_2SO_4.	.001565
3b		Made in our Laboratory from K_2CO_3 and $H_2C_2O_4$.	Recrystallized 6 times. Dried over H_2SO_4.	.001561
4	Eimer & Amend	Eimer & Amend	As received, but dried over H_2SO_4.	.001568
5	Richards & Co.	E. Merck	As received, but dried over H_2SO_4.	.001572
6	Landenberger	E. Merck	As received, but dried over H_2SO_4.	.001571
7	E.H.Sargent & Co.	E.H.Sargent & Co.	As received, but dried over H_2SO_4.	.001858
8	J. W. Queen & Co.	Baker & Adamson	As received, but dried over H_2SO_4.	.001720
9	J. W. Queen & Co.	E. Merck	As received, but dried over H_2SO_4.	.001563
10	Henry Heil & Co.	E. Merck	As received, but dried over H_2SO_4.	.001574

*Reporter on nitrogen for Association of Official Agricultural Chemists.

† Excess of oxalic acid added before recrystallization.

‡ Was ordered as tetroxalate, and so labeled, but was barely acid in reaction, was nearly the normal oxalate.

a. Character of samples on the market.

An examination of the above figures shows at once that, while potassium tetroxalate is obtainable of a fair degree of purity, the chemical market cannot in this case, as in many others, be depended upon to furnish a strictly chemically pure salt. In discussing the subject, I shall take the result under 3*b* as a standard, believing it to be more accurate than that obtained by comparison with the hydrochloric acid solution standardized by silver chlorid, although this result is placed above the table, that any may refer to it who desire.

Leaving out No. 2, which was ordered in Sept., 1889, and which, when received, turned out to be the almost pure normal oxalate, we find that three, viz.: Nos. 1*a*, 7 and 8 were mixtures of acid potassium oxalate and the tetroxalate, while the other five, four of which were of Merck's manufacture, were practically pure. It is specially noticeable that in no case was there an excess of oxalic acid present, while in Nos. 1*a*, 7 and 8 a sufficient quantity had not been added. Nos. 4, 5, 6, 9 and 10 run quite close together, and are nearly up to the standard of a tetroxalate recrystallized three times after addition of oxalic acid, but each might be somewhat improved by such recrystallization.

b. Preparation of pure potassium tetroxalate.

The preparation is easily and speedily accomplished, either from the tetroxalates as bought, or from potassium carbonate and oxalic acid. In the cases 1*b*, 2*a*, 2*b*, 3*a* and 3*b*, the salt was recrystallized from boiling solution with addition of oxalic acid previous to the first crystallization. In each case the salt came down in well-formed crystals on the natural slow cooling of the solution, the supernatant liquid was discarded, the crystals were washed once by decantation with distilled water, recrystallized again from pure distilled water a sufficient number of times, pressed between filter papers, and dried over night in a desiccator above sulfuric acid. It seems to be advisable to continue the first heating in presence of oxalic acid for at least an hour. This was especially apparent in the case of 3*a*. Sufficient oxalic acid had been added, but the

crystals first formed were a mixture similar to Nos. 1*a*, 7 and 8, and were only purified on further addition and heating with oxalic acid. The last part of the reaction seems to take place slowly, which may account for the trouble in the three impure samples. The work was very easily carried out, three crystallizations being easily made in the course of as many hours with little time taken from other work. In no case was there an excess of acidity or a loss of water of crystallization, either of which would mean a *decrease* in the amount of ammonia found in one cubic centimeter. The fact that this is the case, and that the results compare as they do with those obtained by other methods of standardization, is largely proof of the purity of the salt. If there had been an excess of acidity, as claimed by many members of last year's Association of Official Agricultural Chemists,* the results would be lower than those obtained by silver chlorid, for, *more acid to a certain weight means that a greater number of cubic centimeters of the ammonia solution would be required to neutralize that acid, and consequently one cubic centimeter on calculation would appear to contain less ammonia.* This is contrary to the general concensus of opinion that potassium tetroxalate gives higher results than silver chlorid and taken in connection with the above table of results, leads me to believe that excess of oxalic acid is never a fault in a properly recrystallized or a commercial chemically pure potassium tetroxalate. As the recrystallization of the salt is so easily accomplished, I believe it best for the sake of extreme accuracy to recrystallize more than three times, and the results in 3*b* would seem to indicate this. While the change made by the three extra crystallizations is only slight, I believe it to be worth while to do this extra work as a safeguard, especially as the salt once prepared will be of service for a long time.

c. Does the salt lose or gain water under ordinary conditions?

Potassium tetroxalate loses water of crystallization at 100° quite noticeably, and drying at this temperature is out of the question. Such drying, however, is by no means necessary or even desirable. Fortunately for the purposes of this section I had prepared some

*Bulletin 31. Division of Chemistry, U. S. Dept. of Agriculture, pages 131, 144 and 154.

etroxalate from normal potassium oxalate nearly three years ago. During this time the bottle containing the salt has been opened from time to time and portions removed, but the remainder had not been dried or otherwise tampered with during that time. It gave as removed from the bottle without drying a result, 2*a*, fully as close to that obtained by silver chloride as when the salt was first prepared, fairly within the limits of error, and agreeing closely with the other freshly prepared and three-times recrystallized tetroxalates. This would show that the substance was not hygroscopic, as it had been freely exposed to atmospheric influences. The result given in 2*b*, reached after drying the same crystals for eighteen hours over sulfuric acid, shows that no loss of water of crystallization took place during three years. In order to test this latter point still further, I placed 6 gms. of broken fragments of crystals of potassium tetroxalate in a desiccator over fresh concentrated sulfuric acid. For several days there was no loss apparent to the balances, but after forty days a loss of one milligram was indicated. This loss, when calculated to the .2 gm. tetroxalate, used in an analysis, amounts to .000032 gm., a quantity much less than any of our balances will show. The loss was now more rapid, but even when the last weight was taken, after three months drying, the loss was insignificant. It was sufficient merely to change the result .001561 to .00156097, just three points in the eighth decimal place. As it is never necessary to dry the tetroxalate over sulfuric acid for more than twelve hours, I think I can safely say that the presence of water of crystallization in this salt is in nowise an objection.

d. On the use of indicators with potassium tetroxalate.

Phenol-phthaleïn, litmus and coralline give a sharp reaction, but phenol-phthaleïn is to be recommended where fixed alkali solutions are to be titrated against.

Litmus prepared according to Sutton gives a sharp reaction with ammonia solution. The change of color should be from acid to alkaline, and the point taken is the *distinct appearance of the blue.* The shade of red begins to change before this point is reached, but the appearance of the blue is sharp and not to be mistaken. Well agreeing results can be obtained with varying quantities of

tetroxalate, which would not be the case if the change were [illegible] ful. Coralline also has a fairly sharp reaction but does not equal litmus in this respect.

Cochineal becomes decidedly alkaline in color several tenths of a cc. before this point is reached with any of the preceding and cannot be used.

Di-methyl-anilin orange and turmeric change gradually during the addition of many cubic centimeters of alkali, and the first becomes fully alkaline in color when the tetroxalate is [illegible] neutralized. As has long been known, this indicator cannot be used with organic acids, nor does this case prove [illegible] exception.

ACID POTASSIUM TARTRATE

By Charles E. Parsons

H. Borntrager (*Chem Zeit*, 1881, p. 510), H. Hebebrand (*Z. f. anal. Chem.*, 1892, p. 226), and A. Borntrager (*Z. f. anal. Chem.*, 1892, p. 5[illegible]), have recommended acid potassium tartrate as a means for the standardization of acid and alkali solutions. In order to try this salt, I made up some according to the directions given by the last named person, but [illegible] necessary, in order to get the pure salt to crystallize [illegible] addition.

The following are the results obtained:

Prepared according to directions, [illegible] NH_4 [illegible]	[illegible]
Recrystallized twice	[illegible]
Recrystallized three times	[illegible]
Per potassium tetroxalate	[illegible]

Good results were obtained with the pure salt. The reaction with litmus was, however, not so sharp as with tetroxalate, and a number of determinations must be made with the salt to be sure of results. It has also the disadvantage of being much more tedious to prepare than the tetroxalate, and [illegible]

goes shows no advantages whatever over the latter.

The tendency in the above is to retain an excess of acid, probably tartaric, set free in small quantity by the hot hydrochloric acid. The acid tartrate was washed after boiling with hydrochloric acid until the latter had been completely removed.

THE PRECIPITATION OF PHOSPHO-MOLYBDATE OF AMMONIA IN THE PRESENCE OF ARSENIC.

By H. C. Babbitt.

Unquestionably many of the discrepancies in phosphorus determinations by molybdate methods may be traced to the presence of arsenic and the precipitation of the phospho-molybdate at so high a temperature that a portion, at least, of the arsenic is precipitated. To illustrate this point, the following experiments were made: To one gram of steel (phosphorus = .006, arsenic nil) .0133 gm. of arsenic in the form of sodium arsenite was added. The sample was dissolved in nitric acid, oxidized with potassium permanganate; in fact, treated as an ordinary phosphorus determination, the As_2O_3 by this treatment being oxidized to As_2O_5. Ammonium molybdate was added (Wood's 1888 formula), and the precipitation made at the following temperatures:

Precipitated at 85° C.	= .0100 gm.	arsenic	=	75.2%	of arsenic	added.
" " 70° C.	= .0085	"	"	= 63.9%	"	"
" " 60° C.	= .0016	"	"	= 12.0%	"	"
" " 50° C.	= .00104	"	"	7.8%	"	"
" " 40° C.	= .00104	"	"	= 7.8%	"	"
" " 35° C.	= .00057	"	"	= 4.3%	"	"
" " 30° C.	= .00033	"	"	2.5%	"	"
" " 25° C.	= .00003	"	"	= .2%	"	"

As the amount of arsenic precipitated at 25° C. is within the limits of experimental error, the conclusion drawn from these experiments is, that if the temperature of precipitation is kept at or below that point, the presence of arsenic has no influence on the accuracy of phosphorus determinations, while above that temperature there is a possibility of suspicion.

Wellman Iron and Steel Co.,
Thurlow, Pa.

Oxygen. Leduc, oxidizing hydrogen over copper oxide, Dumas' method, with special precautions and all corrections applied, gets the following results for this constant:

[illegible]

Compt. Rend. **115**.

Nickel and Cobalt. A few experiments upon the weights of these metals have been recorded by Schutzenberger. First, pure $NiSO_4$, dried at 44[illegible], was reduced by hydrogen:

[illegible]

Secondly, pure NiO was reduced by hydrogen to metallic nickel:

[illegible]

One similar experiment with cobalt oxide gave [illegible]:

[illegible]

The results given for the atomic weights are [illegible] Schutzenberger [illegible] *Compt. Rend.* **114**, [illegible].

Cadmium. Morse and Jones have determined the weight of this metal by two methods, the first being to reduce cadmium distilled in a [illegible] specimen [illegible].

First, cadmium was [illegible] latter was reduced to [illegible] oxide thus obtained gave [illegible] lower results:

[illegible]

Morse and Jones [illegible]

The second method was that used by Lenssen and by Partridge, and consisted in igniting cadmium oxalate to oxide. As the oxalate is very hygroscopic, great care was taken to dry it thoroughly before weighing. Five experiments were made, as follows:

							O = 16. C = 12.001.
1.55937	gms.	oxalate	gave	.98526	gms.	oxide.	Cd = 112.026.
1.77483	"	"	"	1.13582	"	"	" 111.981.
1.70211	"	"	"	1.08949	"	"	" 112.049.
1.70238	"	"	"	1.08967	"	"	" 112.051.
1.74447	"	"	"	1.11651	"	"	" 112.019.
							Mean, Cd = 112.025.

—*Doctoral Dissertation* by H. C. Jones, Baltimore, 1892. Also, *Am. Chem. J.* **14**, 261.

The atomic weight of cadmium has also been measured by Lorimer and Smith, who precipitated the metal electrolytically from a cyanide solution of the oxide. Nine experiments gave values as follows, when O = 16:

.34767	gm.	CdO	gave	.30418	gm.	Cd.	Cd = 111.908.
.41538	"	"	"	.36352	"	"	" 112.156.
1.04698	"	"	"	.91618	"	"	" 112.148.
1.04066	"	"	"	.91500*	"	"	" 111.924.
1.26447	"	"	"	1.10649	"	"	" 112.064.
.78493	"	"	"	.68675	"	"	" 111.917.
.86707	"	"	"	.75884	"	"	" 112.182.
.67175	"	"	"	.58785	"	"	" 112.105.
1.44362	"	"	"	1.26329	"	"	" 112.087.
							Mean, Cd = 112.055

—*Ztschr. anorg. Chem.* **1**, 364.

Boron.—The posthumous paper upon the atomic weight of boron, by the late J. L. Hoskyns-Abrahall, edited by T. Ewan and P. J. Hartog, has at last been published. First, by ignition of borax, $Na_2B_4O_7.10H_2O$, the following results were obtained:

Per Cent. of Water.	Atomic Weight of Boron.
47.2069	10.843
47.3308	10.593
47.3504	10.554
47.2763	10.703
47.2686	10.719

*Possibly a misprint for .91050?

This method is obviously not to be trusted. Better result secured by titrating the bromide, BBr_3, with a solution of essentially after the general method of Stas. From 1 [illegible] gms. of bromid were taken for each experiment. Final as follows:

Preliminary Series.		Final Series.
B =	10.902	10.764
	10.908	10.762
	10.887	10.838
	10.860	10.826
	10.870	10.831
		10.826
		10.811
		Mean 10.817, ± .047

Mean of the last five, which the authors considered the 10.827, ± .003.

Calculated with Na = 23.051, Ag = 107.923,
Br = 79.951, O = 16, and H = 1.007[illegible].

J. Chem. Soc. **61**, 650. August 1

Palladium. Atomic weight redetermined by Bailey and L After some unsatisfactory experiments with palladious cy palladammonium cyanide, and palladious potassium chlorid palladammonium chloride, $Pd(NH_3Cl)_2$, was selected as the salt for the purpose of the authors. First the salt was reduc ignition in a stream of hydrogen, and the ammonium chlo formed was collected and estimated as silver chloride.

Salt taken.	AgCl found.	At. wt. Pd.
2.2270	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
	Mean	[illegible]

With Ag = [illegible] N = [illegible] H

Second, the salt, $Pd(NH_3Cl)_2$, [illegible] hydrogen [illegible] during the heating [illegible] Sprengel vacuum [illegible] gas could be withdrawn.

	Percentage of Pd in $Pd(NH_3Cl)_2$.	At. Wt. Pd.
Series A	50.1426	105.353
	50.1698	105.468
Series B	50.0878	105.123
	50.2376	105.754
	50.1671	105.359
	50.2184	105.672
Series C	50.2132	105.651
	50.1621	105.435
	50.1224	105.267
	50.1838	105.523

Mean of series A, Pd = 105.410
" " " B, " 105.508
" " " C, " 105.458
General mean, " 105.459

J. Chem. Soc. **61**, 745.

ESCHKA'S METHOD OF DETERMINING SULFUR.*

BY F. HUNDESHAGEN.

In determining sulfur by the method of Eschka a mistake may arise by the volatilization of a part of the sulfur, even when more than the prescribed proportion (½ times) of the dried mixture of magnesia and sodium carbonate is added, and when the coal and magnesia-soda mixture are finely ground and intimately mixed and with cautious heating under certain conditions a considerable loss of sulfur may be experienced, sometimes as much as 6 per cent. of the amount present. With an imperfectly dried mixture and careless heating the loss may be still greater.

The evolution of the volatilile sulfur compounds may be detected by the blackening of a wet piece of paper soaked in a solution of lead with which the crucible is covered. Many coals, rich in sulfur, give by heating with the magnesia-soda mixture such an amount of hydrogen sulfid or ammonium sulfid, that black glistening crusts of lead sulfid form in a few seconds on the paper, and these appear again on changing the paper.

The volatilization of sulfur ceases entirely, or almost entirely, if potassium carbonate be used partly or wholly in place of sodium carbonate. I found a mixture of two parts magnesia and one part calcined potassium carbonate satisfactory in all cases. (More than one part potassium carbonate to two parts magnesia cannot be

*Translated from the Chemiker Zeiting, July 27, 1892.

used as the mass balls on heating and prevents complete combustion of the coal.)

To one part of coal at least two parts of the dry mixture are taken of which three-fourths are mixed with the coal in a good-sized crucible and the remaining fourth placed over the surface evenly and the process carried out in the usual way. The combustion is more rapid than with the soda mixture, and is usually finished in one-quarter to one-half hour. This mixture is also less dusty than the soda mixture.

Even with very sulfurous coals, no noticeable amount of sulfur is lost when the potash mixture is used.

The following results were obtained by burning three Bohemian brown coals rich in organic sulfur. *A* by Eschka's method, *B* with the 2 : 1 magnesia-potash mixture; they show what sulfur may be lost when working with the first method. In both series two parts of the mixture were used for one of coal; the ignited mass was treated, as Muck prescribes, with bromin and hydrochloric acid, and the filtrate precipitated with barium chlorid. The small amount of sulfur in the reagents was subtracted in the calculations.

With Nos. 1 and 2 coals the mixture was freshly dried; with No. 3 treated with about 20 and 15 per cent. of water. In the latter cases the heating of the coal was somewhat more rapid.

	A. Magnesia Soda Mixture.		*B.* Magnesia Potash Mixture.		
	Action on Lead Paper.	Sulfur Found.	Action on Lead Paper.	Sulfur Found.	Loss of Sulfur in *A*
Brown Coal No. 1	Blackening	1.97%	No coloration	2.10%	0.13%
" " " 2	"	2.43%	"	2.58%	0.15%
" " " 3	"	2.77%	"	3.06%	0.29%

Further experiments showed that a mixture of two parts magnesia one-half part sodium carbonate and one-half part potassium carbonate, even when slightly moist, answers the purpose perfectly. These experiments show the necessity of replacing the sodium carbonate in Eschka's mixture partly or wholly by sodium carbonate.

The imperfect action of Eschka's mixture is due in the first

place to the property of sodium carbonate of becoming anhydrous at a low temperature. In this condition it has very little absorbsorbing power for hydrogen sulfid. It is also due to the ease with which sodium sulfid is decomposed by carbon dioxide.

The improved behavior of the potash substitute is explained by the property which the later has to retain moisture at a higher temperature and to combine with hydrogen sulfid with the formation of potassium sulfid and carbon dioxide. This absorption is facilitated by the conversion of a part of the carbonate in intimate mixture with magnesia and water into the much more active hydroxid, a property not possessed, or at any rate only in very small degree by sodium carbonate.

How different is the absorptive power of sodium and potassium carbonates for hydrogen sulfid is shown, for example, by the observation that sodium carbonate mixed intimately with a small quantity of sodium sulfid and sodium bicarbonate, especially when heated, gives off hydrogen sulfid in quantity; addition of a proportionately small amount of potassium carbonate when well mixed suffices to hold this in combination, even when heated.

NOTE ON THE PREPARATION OF SAMPLES OF RICH ARGENTIFEROUS LEAD FOR ASSAY.*

By John Pattinson, F.I.C., and H. S. Pattinson, Ph.D., F.I.C.

It has been found that the most satisfactory method of obtaining an average sample of pigs of rich argentiferous lead—containing from 100 to about 1,000 oz. of silver per ton of lead—is to saw each pig through with a circular saw. The fine particles produced by the saw, termed "sawings," are collected, and from them the samples are drawn to be sent to the assayer.

Assays of rich argentiferous lead are best made upon from 200 grains to half an ounce of lead, but such a small quantity of the sawings as this cannot be relied upon to represent the whole bulk of the sample, because of the large size of some of the particles. This difficulty, however, is easily overcome by melting up either the whole of the sample or such a quantity of it as can be relied upon to represent the composition of the whole, and casting the lead into small cakes or "buttons" from which portions weighing

*Jour. Soc. Chem. Ind. Apr., 1892.

from 200 grains to half an ounce can then be cut for assaying. We find that from a sample of sawings of the usual size a button or small bar fairly representing the sample can be cast from about 2,000 grains.

When the sawings are melted the button of lead obtained invariably weighs less than the weight of sawings taken. This loss of weight is partly due to the oxidation of the impurities contained in the lead, which separate as dross or are volatilized during the process of melting. The remaining lead is consequently enriched in silver by the removal of these impurities and the assay obtained from this lead is higher than the true assay of the parcel from which the sawings were taken. A correction must therefore be made upon the assay for this enrichment in order to arrive at the true assay of the sample.

The total loss of weight on melting the sawings is however, not wholly due to oxidation and volatilization of the impurities but is partially due to the combustion of the oil that is upon the surface of the sawings, which has been introduced into the sample by the necessity of using oil to lubricate the circular saw. This increases the assay of the melted lead by an amount corresponding to the *total* loss of weight on melting the sawings, would therefore be obviously wrong. Since a portion of this loss is due to oil on the sample which was no part of the original parcel of lead. The percentage of oil in the sawings must therefore be determined and deducted from the total percentage loss on melting the sawings.

We determine the oil in the sawings by washing a weighed quantity of them with ether, filtering into a tared flask, evaporating the ether and weighing the oily residue remaining in the flask.

With some classes of lead the loss of weight due to oxidation and volatilization of the impurities when the sawings are melted alone is very considerable. We find that a very small addition of dimorphic potassium chlorate, a little potassium cyanide, to the sawings when they are melted. We use [illegible] about half an ounce of dimorphic potassium chlorate [illegible] grains of the sawings [illegible] the melting [illegible] crucible.

As an example [illegible] shows how the [illegible] stance may be [illegible]

4,000 grains of sawings melted alone lost in weight 60 grains = 1.5 per cent.

2,000 grains of the same sawings melted with KCN lost 16 grains =0.8 per cent.

The percentage of oil in these sawings was determined and found to be 0.52 per cent. Deducting this amount from each of the above total losses we find that the loss due to oxidation and volatilization is—

When the sawings are melted alone, 0.98 per cent.

When the sawings are melted with KCN, 0.28 per cent.

In this instance, therefore, the loss due to oxidation and volatilization was 3½ times greater when the sawings were melted alone than when they were melted with potassium cyanid.

The following table gives some examples of the results obtained with several samples of sawings when potassium cyanid was used in melting them :—

	Total Percentage Loss including Oil	Percentage Loss due to Oil	Percentage Loss exclusive of Oil
1. First trial	0.78	0.52	0.26
Second trial	0.80	0.52	0.28
2. First trial	0.35	0.11	0.24
Second trial	0.35	0.11	0.24
3. First trial	0.50	0.32	0.18
Second trial	0.51	0.32	0.19
4.	0.30	0.15	0.15
5.	0.30	0.13	0.17
6.	0.31	0.12	0.19
7.	0.38	0.15	0.23
8.	0.25	0.10	0.15
9.	0.33	0.14	0.19

It will be seen, from the tests of the first three samples, which were made in duplicate, that very concordant results are found by this process, and also that, in all the samples, the loss of weight due to the oil is very considerable as compared with the loss from other causes. In some instances the loss due to oil is about twice as much as the loss from oxidation and volatilization.

The amount of loss from oxidation and volatilization in all these samples is but small, varying from 0.15 to 0.28 per cent., and it may seem at first sight to be of little importance, but, actually, the correction of the assay corresponding to these small losses

makes a difference on a lead containing, say, 500 oz. of silver per ton, of ¾ oz. of silver per ton in the first case, and 1 oz. 8 dwt. per ton in the latter case; and these amounts when deducted from the assays of the cakes of lead give the true contents of silver in the original lead. With richer leads the correction is, of course, proportionally greater.

It is obvious that in the above cases, if the correction for loss on melting the sawings were to include also the loss due to the oil, an error would be made which would lead to an *excessive deduction* varying from ½ oz. to 2 oz. 12 dwt. of silver per ton, supposing the lead to contain 500 oz. of silver per ton by assay of the cake of melted sawings.

DISCUSSION.

Mr. SHAW suggested that liquation and separation of constituents might take place in the small ingot, but Mr. PATTINSON considered that it was too small and cooled too quickly for that to occur to any measurable extent.

Mr. RENOLDSON thought that if the oil were first removed, its amount need not be determined; he also suggested the use of water as a lubricant in place of oil.

THE INTERNATIONAL CONFERENCE ON CHEMICAL NOMENCLATURE.*

BY HENRY E. ARMSTRONG.

At the meeting of the International Chemical Congress, held in Paris in the summer of 1889, a special Section was appointed to consider the unification of chemical nomenclature, and, after discussing a variety of propositions, some of which were adopted, it was decided to form an International Commission for the further study of the subject.†

The members resident in Paris, having been constituted a permanent committee of the Commission, have devoted an immense amount of time and care to the preparation of a scheme, and it was to discuss their report‡ that we met at Geneva on Easter

*Nature, May, 1892.

†The following chemists eventually consented to serve on the Commission: Messrs. Béhal, Berthelot, Bouveault, Combes, Fanconnier, Friedel, Gautier, Grimaux, Jungfleish, Schutzenberger (all representing France), Graebe (Switzerland), Alexejeff and Beilstein (Russia), von Baeyer and Nölting (Germany), Lieben (Austria), Paterno (Italy), Franchimont (Holland), Armstrong (England), Istrati (Roumania), Calderon (Spain), Cleve (Sweden), Boukowski Bey (Turkey), Ira Remsen (United States), and Mourgues (Chili).

‡This report had been prepared by the following: Messrs. Friedel (President), Béhal, Bouveault, Combes, Fanconnier, Gautier, and Grimaux.

Monday last. The French Committee had issued invitations, not only to members of the Commission, but also to many other prominent chemists, so that the meeting was a thoroughly representative one. It is worth mentioning, as an illustration of the sympathetic treatment accorded by public bodies in France to men of science, that the Paris-Lyons-Marseilles Railway Company granted a reduction of one-half of the fare over their line to members of the Congress.

Very happily, the local committee had arranged that all might stay at the one hotel—the Métropole—and it was here that we first met in friendly union on the Monday evening.* The next morning the Congress assembled at the Hotel de Ville, M. Richard, the Cantonal Minister of Education, being in the chair. After an admirable address of welcome from this gentleman, who appeared to thoroughly appreciate the importance of the object in view, on the motion of Prof. Canizzaro it was wisely decided not to follow the complimentary, but somewhat unbusinesslike Continental practice so frequently adopted, of appointing a different chairman each day, but to have only one. M. Friedel, who had taken the chair at all the numerous meetings of the Paris Committee, having been chosen by acclamation President of the Conference, formal business was at once entered into, and, after the necessary interval for lunch, the sitting was resumed in the afternoon. We met in like manner on the two following days, and the final sitting took place

*The following is the official list of those who took part in the Conference: Messrs. H. E. Armstrong, Professor at the Central Institution, London, Secretary of the Chemical Society; A. Arnaud, Professor at the Museum, Paris; Adolphe von Baeyer, Professor at the University of Munich; Barbier, Professor at the Faculty of Sciences of Lyons; Aug. Béhal, Professor at the Superior School of Pharmacy of Paris; Louis Bouveault, Doctor of Science, Paris; Stanislas Canizzaro, Professor at the University of Rome; Paul Cazeneuve, Professor of the Faculty of Medicine of Lyons; Alphonse Combes, Doctor of Science Paris; Alphonse Cosso, Director of the Experimental Station of Agriculture, at Turin; Maurice de Lacre, Professor at the University of Gand; Michel Filetti, Professor at the University of Turin; Emil Fischer, Professor at the University of Würzburg; A. P. N. Franchimont, Professor at the University of Leyden; Charles Friedel, Member of the Institute, Professor at the Sorbonne, Paris; Dr. J. H. Gladstone, F.R.S., London; Carl Graebe, Professor of the University of Geneva; Phillippe-Auguste Guye, Professor at the University of Geneva; Istrati, Professor at the University of Bucharest; Albert Haller, Professor of the Faculty of Science of Nancy; Maurice Hanriot, Fellow-Professor of the Faculty of Medicine, Paris; A. R. Hantsch, Professor at the Polytechnic School of Zurich; Achille Le Bel, Doctor of Science, Paris; A. Lieben, Professor of the University of Vienna; Leon Maquenne, Doctor of Science, Assistant Naturalist at the Museum, Paris; von Meyer, Professor at the University of Leipsic; Denis Monnier, Professor of the University of Geneva; R. Nietzki, Professor of the University of Bale; Emilio Noelting, Director of the School of Chemistry of Mulhouse; Emmanuel Paterno, Professor at the University of Palermo; Amé Pictet, Instructor at the University of Geneva; William Ramsay, F.R.S., Professor of the University of London; Zdenko-H. Skraup, Professor of the University of Graz; Ferdinand Tiemann, Professor of the University of Berlin.

The Local Committee was composed of the following: Messrs. Emile Ador, H. W. de Blonay, Alex. Claparede, Prof. C. Graebe, Prof. Ph. A. Guye, Alex. Le Royer, Prof. Denis Monnier, Amé Pictet, Fred. Reverdin, Prof. Albert Rilliet, Edouard Sarasin.

on the Friday morning, but many had left before this. On Tuesday evening, by invitation of the local committee, we visited the theater, a very beautiful building. On the Wednesday evening, we were entertained by them at a dinner at the Hotel Métropole, on which occasion a very striking speech was delivered by Prof. von Baeyer, who, after pointing out that experimental chemistry had been carried, early in the century, into Germany from France by Liebig, who was tutored by Gay-Lussac, proceeded to say that, although the science had now undoubtedly reached its highest development in Germany, it was more than probable that, in the future, circumstances would arise which would lead to some other nation—France, Russia, Italy, or England—coming to the fore. On this occasion, on the motion of M. Le Bel, it was unanimously decided to appoint M. Marignac Honorary President of the Congress, and a letter to him expressing our regret that ill-health prevented his taking part in its work was at once signed by all present. We were indebted in many other ways to the local committee, and there is no doubt that the success of the meeting was in large measure due to the forethought and hospitable care exercised by them on our behalf. Absolute amity prevailed throughout, and it was clear that all were bent on co-operating to secure the carrying out to a successful issue of a very difficult but most important work. The great advantage to be derived from the personal intercourse which such meetings promote was soon apparent; gradually, the doubts which many entertained as to the possibility of devising a practical, rational scheme of nomenclature were dispersed, and ere many hours had elapsed the sympathies of all present were enlisted on behalf of the work; thus a mission has been sent forth which will explain the enterprise to chemists generally.

The resolutions passed at the meetings are appended to this article. These, I think, are in no way to be taken as in all respects final, but they will serve to prepare the way and to indicate the lines on which the work is to be carried out. The position in which we found ourselves placed, in fact, was not one which justified our arriving at decisions which could fairly be regarded as binding. The report of the French Committee was placed in our hands only on the morning of the first meeting, and it was impos-

sible to master its contents at so short a notice, and still less to criticise and test the application of its recommendations in detail. That the scheme would serve but as the basis for discussion was soon evident, when at the very outset a system of nomenclature for the hydrocarbons was adopted very different and far more significant than that recommended in the report; and numerous other departures from its recommendations were carried in the course of the proceedings. Again, some of the most active members of the Congress had confessedly paid attention only to special groups of compounds, and had not tested the application of proposals which they strenously? advocated to compounds of other groups; but as a nomenclature admirably adapted to one class may be open to all sorts of objections when applied to another, the general bearing of recommendations made with reference to special groups will have to be fully considered before they can be finally adopted. The resolutions relating to fatty acids (Nos. 18, 19,) are of this kind, and their adoption was warmly opposed by an important minority on the ground that, however well they might be adapted to acids pure and simple derived from open-chain hydrocarbons, their application to acids derived from closed-chain hydrocarbons and acids containing other radicles in addition to carboxyl was beset with difficulty. In order to name an acid in accordance with this resolution, the formula of the corresponding hydrocarbon must be constructed from that of the acid by changing carboxyl into methyl; for example, citric acid, $CH_2(CO_2H).C(OH)(COOH).CH_2(COOH)$, would have to be regarded as a derivative of methylpentane, and would be named methylpentanoltrioic acid, numerals being added to indicate the positions of the hydroxyl and carboxyl groups; in like manner, mellitic acid, $C_6(COOH)_6$, would be named hexamethyl-benzenehexoic acid, although no methyl is present in it. The mental effort involved in visualizing the formulæ from such names as these would appear to be far greater than if they were respectively named propanoltricarboxylic acid and benzenehexacarboxylic acid, or simply propanoltri-acid and benzenehex-acid, the use of the term *acid* being understood to imply the presence of carboxyl. A decision on points such as these can only be arrived at after careful study of the general effect of such a proposal, and there was no time for such a comparison during the brief debate

possible at a Conference. In some cases, there [illegible] that the full force of objections raised to proposals [illegible] a majority subsequently voted was not felt, owing [illegible] which necessarily arises at an international Conference [illegible] guage used be not equally familiar to all present [illegible] full expression can not be given by all to their views. M[illegible] although it is easy to criticize destructively [illegible] constructive criticism under such circumstances [illegible] consequently a proposal may be accepted [illegible] objections to its adoption simply because nothing [illegible] suggested at the time. An instructive case of [illegible] discussing thio compounds. The proposals in [illegible] not regarded as altogether satisfactory [illegible] suggested and carried which to many appeared [illegible] the next morning, when the time came to [illegible] arrived at on the previous day, the discussion was [illegible] slight modification of the original proposal was [illegible] was recognized to be an improvement and the [illegible] lution was rescinded. Clearly at such meetings [illegible] pend on the right expression being found by happy [illegible] at the right moment.

The one resolution which covers all others [illegible] nature of the task to be undertaken is the first. W[illegible] we may choose to apply [illegible] an absolute necessity at the times that [illegible] bear [illegible] name of such [illegible] translated into the corresponding [illegible] corresponding to any part of [illegible] may [illegible] may [illegible] or have been [illegible] clature [illegible] estimated [illegible] will [illegible] [illegible]

both purposes. There can be little doubt, however, that the future student will cut the knot by declining to burden his memory with a double vocabulary in the case of all but the commonest substances, and that therefore there is but one course open to us (cf. Res. 26).

Although sufficiently conservative to retain methane, ethane, propane, and butane, the Congress decided not to adopt the proposal to continue the use of the names formic, acetic, propionic, and butyric for the first four acids of the acetic series, which was advocated by a substantial minority on the ground that their retention would facilitate the change from the old to the proposed new system. This is one of the questions demanding careful consideration. Many will, no doubt, prefer to retain old unsystematic names as far as possible, but it is easy to see that the desire to avoid change may carry us too far in this direction; it will undoubtedly be very inconvenient to the present generation of chemists to abandon familiar and cherished names, but nevertheless it may be a wise course to boldly face the difficulty, rather than inflict on coming generations a partially illogical and unsystematic nomenclature. The argument that the present familiar names may still be used colloquially is, as I have already said, scarcely a justification of the dismissal of such names from the official nomenclature, as our successors may be expected to object more and more decidedly to a multiplex system as chemical science progresses, and to insist on the adoption of the official as the sole system; the extent to which familiar trivial names shall be retained in the official system is therefore a matter of great importance.

As one aim and object must be to devise a system which is significant and logical throughout no considerations must be allowed to prevail which will defeat this, and it will not suffice to quote present usage in support of illogical proposals; but this has been done. Thus the Congress decided (Res. 46) to name compounds of the type $R'.N_2.R'$ *azo*-compounds, while retaining the name *diazo*-chlorid for $C_6H_5.N_2Cl$. It matters not to us that the manufacturers have chosen to call the colors derived from *diazo*-compounds azo-dyes; if substances such as $(C_6H_5)_2S$ are termed *thio*, and compounds such as $(C_6H_5)_2S_2$ *di*-thio compounds (Res. 43), we are

illustration of the [illegible]
favor of what may fairly be termed popu[illegible]
require to be most carefully guarded against [illegible]
of our system are to harmonize

It will be gratifying to English chemists that the [illegible]
vocated for many years past by our Chemical Society [illegible] in its "Instructions to Abstractors" that particular [illegible]
should be regarded as in the [illegible]
therefore be restricted to particular [illegible]
legalized in extended by the Congress. This [illegible]
importance as we may expect it will [illegible]
and that in future names will be given [illegible]
will to a certain extent [illegible]
confusion which [illegible]
for example [illegible]
many cases [illegible]
formula [illegible]
hoped [illegible]

But the [illegible]
fully [illegible]
attack [illegible]
properties [illegible]
though [illegible]
its [illegible]
would [illegible]
[illegible]

not yet so far advanced as to make this possible or even desirable, and it would be most unfortunate if Beilstein were at the present juncture to promulgate a system which is manifestly incomplete; nothing can be worse in such a case than to consent in haste, when it is evident that this would surely involve repentance at leisure.

Those of us who are interested in the work, and competent to advance it, must now test in detail the application of the proposals which have been provisionally adopted, and we must assist in contributing to the ultimate establishment of a system on the broad lines of policy laid down for our guidance at the Congress. As it is not improbable that in the future, owing to the extended use of our language, the major proportion of chemical students will speak English, it is essential that due attention be paid to the matter here in England, so that a system may be devised which we can make use of without difficulty.

Resolutions taken by the Congress.

1. In addition to the usual methods of nomenclature, an *official* name, permitting of distinguishing each body under a distinctive title, will be established. The Congress requests authors to mention in their articles the official name in parenthesis, in addition to the name chosen by them.

2. It is decided to consider, for the present only, those bodies of a known constitution, leaving for later consideration bodies of unknown constitution.

3. The termination *ane* is adopted for all the saturated hydrocarbons of the fatty series.

4. The old names of the first four saturated hydrocarbons (*methane*, *ethane*, *propane*, *butane*) are retained; the names derived from the Greek numbers will be used for those which have more than four atoms of carbon. These names will distinguish the normal hydrocarbons.

5. The hydrocarbons with an open chain are regarded as derivatives of the normal hydrocarbons, and their name will be derived from the longest normal chain that can be established in their formula.

6. The numbering of the lateral chains will be drawn from the atom of terminal carbon nearest in a lateral chain; in the case where the lateral chains nearest to the extremities will be placed symmetrically, the simplest will decide the choice.

7. Whenever a residue is substituted in a lateral chain, *metho-*, *etho-*, are employed instead of *methyl-*, *ethyl-*, prefixes reserved for the case where the substitution takes place in the principal chain.

8. In the hydrocarbons having only one *double bond*, the termination *ane* of the corresponding saturated hydrocarbon will be replaced by the termination *ene* (ex. ethene); in those having two *double bonds*, the termination *diene* will be used (ex. propadiene); those having three, *triene*, etc. If it is necessary, the place of the double bond is indicated by the number of the first atom of carbon to which this double bond is attached.

9. The names of the hydrocarbons with [illegible] will be [illegible] in like manner with *ene*, *diene*, *triene* [illegible] for [illegible] allylene, hexadiene for dipropargyle

10. In the case where occur simultaneously both [illegible] the terminations *ene*, *diene*, etc. will be employed

11. The saturated hydrocarbons with a closed chain will take the [illegible] of the corresponding saturated hydrocarbons of the fatty series preceded the prefix [illegible] ex: cyclohexane for hexamethylene

12. The atoms of carbon in a lateral chain will be [illegible] same number as the atom of carbon to which the [illegible] will carry a number which will indicate their distance [illegible] tachment in the lateral chain

In the case where two chains are attached to the same [illegible] the numbers of the most simple among them will be [illegible]

The same method of numbering is adopted [illegible] closed chains

13. The non saturated hydrocarbons will [illegible] ing saturated hydrocarbons. In case [illegible] chain the number will be placed before the [illegible] to the bond highest in order

14. The numbering of the hydrocarbons is [illegible] tion products

15. The alcohols and the phenols will be called [illegible] drocarbons from which they are derived terminated [illegible] pentanol, pentanol, etc.

16. Concerning the polyatomic alcohols and phenols [illegible] *di*, *tri*, etc. following the order of the [illegible] between the name of the hydrocarbon [illegible] propane triol for glycerin

17. [illegible] tinguished by the suffix [illegible]

18. In the [illegible] forming an integral part [illegible]

19. The name of [illegible] that of the corresponding [illegible]

The polyatomic [illegible]

2. [illegible] chain [illegible]

2. [illegible] chain, the carbon [illegible]

22. [illegible]

[illegible]

II [illegible]

The oxy-ethers will be designated by the names of the hydrocarbons which compose them, united by the term *oxy-* (ex. pentane-oxy-ethane for ethyl or amyl oxid).

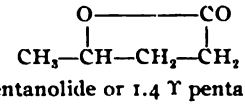
24. The anhydrides of the acids will retain their present mode of designation after the name of their acids (ex. anhydride ethanoic).

25. (12 *bis.*) In the case of two lateral chains attached to the same atom of carbon, the order in which these are expressed will correspond to their degree of complication.

26. A more exhaustive discussion of the bodies with complex functions is postponed, and the study of this question is referred to the International Commission, in order that it may prepare upon this point a plan which will be laid before the next Congress. The Commission will endeavor to reconcile the exigencies of the spoken nomenclature with that of a terminology applicable to the dictionaries.

27. The customary methods for the salts or compound ethers are retained.

28. The lactones will be designated by the word *olide*, indicating that it is an internal anhydride of alcohol and acid. The position of the alcoholic function, as to the carboxyl of the acid alcohol whence proceeds the lactone, can be expressed by the Greek letters α, β, Υ, δ, in addition to the usual numbering of the lateral chains:



1.4 pentanolide or 1.4 Υ pentanolide.

29. The lactonic acids derived from bibasic acids will be named after the lactones from which they are derived, adding the suffix *oic*, characteristic of the acids.

30. The discussion of the closed chains is postponed until the publication of the ideas of Mr. Armstrong upon this subject, will permit the International Commission to compare them with the propositions of Mr. Bouveault.

31. In the aromatic series and all the bodies containing a closed chain, all the lateral chains will be considered as substituting.

32. Aldehydes will be distinguished by the suffix *al* (methanal, ethanal).
Sulfo aldehydes: suffix *thial*.

33. Acetones: suffix *one* ($CH_3.CO.CH_2.CH_3$, butanone 2).
Diacetones, triacetones: suffixes *dione*, *trione*.
Sulfoacetones: suffix *thione*.

34. Quinones: The suffix *quinone* for the bodies homologous to ordinary quinone.

The bodies having the chain CO.CO several times will be diquinones or triquinones.

35. Ammoniacal compounds: no change (ex. ethylamine, ethene-diamine).
The bodies where the bivalent group—NH—closes a chain formed of positive radicals will be called *imines* (ex. ethene-imine).
Phosphines, arsines, stibines, sulfines: the nomenclature in use is retained.

36. Hydroxylamine: this name is retained.

37 Oximes: will be designated by following the rules at present admitted: the *isonitroso* bodies will be called oximes.

(Ex. $CH(NOH).CH_2.CH_2CH_3$ 1 Butanoxione.
$CH_3.CH_2C(NOH).CH_3$ 2 Butanoxime.)

38. Amides: this name is retained: ex: ethanamide

$NH_2CO.CH_2.CH_2.CO.NH$ Butanediamide
$COOH.CO.CH_2.CH_2.CO.NH$ Butanamidic acid

Imides: will be retained.
Amidoximes: this name will be retained.

Ex: $CH_3.C(NOH).NH_2$ Ethanamidoxime

Urea: the generic word *urea* will be retained, and will be employed as suffix for the alcoholic derivatives of urea, which the derivatives from substitution will be called *ureide*.

The bodies containing two molecules of urea will be distinguished by suffixes *diureide*, *triureide*. The acid ureides will take the name *ureic*. The terminations *ureum* and *ureic* are abandoned.

39. Amidines: this suffix will be retained.

Ex: $CH_3.C(NH).NH_2$ Ethanamidine

For the derivatives the name will be doubled, and the name of the substituting group will be preceded by either amino or imino, as the case may be.

Ex: $CH_3.C(NCH_3).NH.NH_2$ Ethanamino-methylimino-[illegible]
$CH_3.C(NH).NH.NHCH_3$ Ethanethylamino-[illegible]

Guanidines: the generic word *guanidine* is retained. Acid guanidines will be named as acid ureides, the derivatives of guanidine being named as [illegible]

40. Betaines: suffix [illegible]

Ex: $N(CH_3)_3.CH_2.CO$ Ethanolbetaine methylbetaine

$CH_2.CO$

41. Nitriles: the prefix [illegible] suffix [illegible] series.

42. Carbylamines: [illegible]

43. Sulfides: [illegible]

Ex: $CH_3.S.CH_3$ [illegible]

Sulfides will be [illegible] compounds [illegible]

Ex: $CH_3.S.CH_3$ [illegible]

Disulfides will be [illegible]

44. [illegible] Water will [illegible] will [illegible]

[illegible]

45. [illegible]

46. [illegible]

Ex: $CH_3.N$ [illegible]
$CH_3.N$ [illegible]
$CH_3.N.CH_3.N$ [illegible]

A METHOD FOR THE IODOMETRIC DETERMINATION OF NITRATES.*

By F. A. Gooch and H. W. Gruener.

It has been shown by DeKoninck and Nihoul† that nitrates may be decomposed completely by the prolonged action of gaseous hydrochloric acid, and determined with accuracy by measuring the iodin set free when the products of decomposition, carefully kept from atmospheric contamination, act upon potassium iodid. These investigators recognized the difficulties attending the use of gaseous hydrochloric acid in analytical processes, and endeavored unsuccessfully to substitute the strong aqueous solution for the gaseous acid. The work to be described in the following account was performed in the search for a simpler method for the iodometric determination of nitrates.

According to a process recently devoloped in this laboratory‡ chloric acid may be determined with the greatest ease. It was shown that in the interaction of a chlorate with potassium iodid, arsenic acid, and sulfuric acid, in regulated quantities in aqueous solution and at the boiling temperature, the first action of the hydriodic acid set free from the iodid by the sulfuric acid is upon the chloric acid, and that not until this action is completed is the arsenic acid attacked and reduced with the simultaneous liberation of a corresponding amount of iodin. If the arsenic acid is taken in quantity sufficient to insure the final decomposition of the entire amount of iodid present, the arsenious acid found at the end of the action is an exact measure of the amount of iodid which escaped the action of the chlorate; and, the quantity of iodid originally taken being known, the amount acted upon by the chlorate, and so the amount of the chlorate itself, becomes known. The arsenious acid is determinable with great accuracy iodometrically, and the chief advantage of the process lies in the fact that the titration is made upon the residue, and that, no collection of the distillate being necessary, the sole apparatus employed in the process proper is an Erlenmeyer beaker and a bulbed tube hung in its neck as a trap to prevent mechanical loss.

*Am. J. Sci., August, 1892.

†Zeitschr. für angewandte Chemie, 1890, p. 477.

‡Gooch and Smith, Am. J. Sci. vol. xlii, p. 220.

This process we endeavored to apply to the determination of nitrates, but under none of the many variations of form and changes of conditions under which we tested it, were we able to secure complete decomposition of the nitrate without so increasing the strength of the sulfuric acid that it was acted upon by hydriodic acid with the consequent unregistered escape of products of decomposition.

The endeavor to substitute a process essentially similar in principle, in which hydrochloric and antimonic acids should replace the sulfuric and arsenic acids, proved likewise unsuccessful.

Abandoning therefore all attempts to so arrange the process that the oxidizing action of the nitrate should be registered in the residue, search was made for a reagent which should be capable of inducing easy decomposition of nitrates (after the manner of ferrous salts in acid solution) and yet (unlike ferrous salts) should be so readily restored to its primitive condition that the products of the oxidizing action of the nitrate should finally pass entirely to the distillate and be registered there. We have found the desired combination of qualities in manganous chlorid dissolved to saturation in concentrated hydrochloric acid. This reagent is acted upon but slowly by nitrates at the ordinary temperature, but, upon warming, the nitrate begins at once to decompose with the formation of a higher chlorid of manganese and liberation of nitric oxid. Ultimately if the heating is continued the chlorid of the higher chlorids is evolved and manganous chlorid remains. During the process of heating the color of the solution passes from the original characteristic green through darker shades to black and returns by the reverse changes to the original tint. The decomposition of the nitrate extends under the conditions to the last traces, but the breaking up of the nitrates with the formation of the higher chlorid, does not take place completely in the presence of water amounting to more than a third of the volume of the solution, and an action already established in strong acid is reversed by the addition of a large amount of water. Chlorates, peroxids, and other substances which liberate oxygen or chlorin when in contact with strong hydrochloric acid induce similar phenomena, but in the absence of such other substances the reaction serves to detect nitrates

when present in fairly small amounts (perhaps one part in sixty thousand) as shown in the accompanying table:

KNO_3 taken.	$MnCl_2.4H_2O$ in strong HCl.	Color developed.
0.01000 gm.	10 cc.	Black.
0.00500	5	Black.
0.00100	5	Dark brown.
0.00050	5	Dark green.
0.00025	5	Deepened tint.
0.00015	5	Deepened tint.
0.00005	5	None.
0.00000	5	None.

In the first attempts to apply this reaction to the quantitative estimation of nitrates, 10 cc. of the manganous mixture, the pure weighed nitrate, and an excess of potassium iodid were put in a tubulated retort fitted with a hollow ground stopper drawn out at both ends so as to serve for the introduction of carbon dioxid evolved in a Kipp's generator charged with marble and acid previously boiled. The neck of the retort passed through a rubber stopper nearly to the bottom of a side-neck Erlenmeyer flask, used as a receiver, in the mouth of which the stopper fitted tightly. The side neck of the receiver was joined by a rubber connector with a bent glass tube passing through a rubber stopper and reaching nearly to the bottom of a side-neck test tube into the mouth of which the stopper was fitted.

The first receiver contained hydrogen sodium carbonate in excess of the amount needed to neutralize the acid in the retort as it should distill over, a considerable quantity of potassium iodid (about 3 gm.) to aid in dissolving condensed iodin, and arsenious oxid in known amount and in excess of the quantity necessary to convert to hydriodic acid the free iodin evolved. The second smaller receiver was partly filled with a dilute solution of potassium iodid and hydrogen sodium carbonate. The current of carbon dioxid was started immediately upon introducing the contents of the retort, and the air was safely removed before the darkening of color, which begins to appear very soon, had spread through the liquid. Heat was applied, and the evolution of nitric oxid and later that of iodin began. The distillation was continued until nearly all the liquid had passed over. Finally, the

contents of both receivers were united and titrated against decinormal iodin. The excess of arsenious oxid remaining unoxidized was taken as the measure of the iodin liberated and, accordingly, of the nitrate decomposed, upon the presumption that two molecules of the nitrate liberate ultimately six atoms of iodin according to the equation.

$$2HNO_3 + 6HI = 4H_2O + 2NO + 3I_2.$$

The choice of the solution for the retention of the halogen evolved was dictated by the consideration, in the first place, that very little iodin could pass through the alkaline arsenite to come into contact with the rubber stopper of the receiver on the way to the second absorbing liquid, and, secondly, that higher oxids of nitrogen reformed by the action of traces of air possibly introduced with the carbon dioxid or imperfectly removed by it could not liberate iodin from an iodid in alkaline solution.

The iodid was introduced into the retort because having chosen to collect the halogen in alkaline solution it became necessary to take steps to break up, before it should reach the receiver, all nitrosyl chlorid, the formation of which our experience in former lines of work not here detailed had led us to expect under the circumstances. In acid solution containing an iodid, nitrosyl chlorid liberates iodin and is registered; in alkaline solution it breaks up with the formation of a chlorid and a nitrite, the latter having no immediate action upon the arsenite. The results of experiments made in this manner are recorded in the accompanying table

Table I.

KNO_3 taken.	KI in retort.	$MnCl_2$ mixture.	KNO_3 found.	Error.
0.1036 gm.	0.8 gm.	10 cc.	0.1009 gm.	0.0027 gm.—
0.1083 "	0.8 "	10 "	0.1082 "	0.0001 " —
0.1064 "	0.8 "	10 "	0.1053 "	0.0011 " —
0.1068 "	0.8 "	10 "	0.1033 "	0.0035 " —
0.0551 "	0.8 "	10 "	0.0531 "	0.0020 " —

The experiments of Table II were carried out in a manner essentially similar to that of the experiments of Table I, excepting the single point that the iodin evolved in the process of decomposition of the nitrate was received in potasssium iodid instead of in an alkaline arsenite. The contents of the receivers were united, made alkaline with hydrogen sodium carbonate, treated with an

excess of decinormal arsenious acid, and the unoxidized arsenious acid was determined by decinormal iodin.

Table II.

KNO_3 taken.	KI in retort.	$MnCl_2$ mixture.	KNO_3 found.	Error.
0.2039 gm.	1.6 gm.	20 cc.	0.2025 gm.	0.0014 gm.—
0.1060 "	0.8 "	10 "	0.1035 "	0.0025 " —
0.1036 "	0.8 "	10 "	0.1016 "	0.0020 " —
0.1013 "	0.8 "	10 "	0.1002 "	0.0011 " —
0.0521 "	0.5 "	10 "	0.0521 "	0.0000 " —
0.0235 "	0.5 "	5 "	0.0227 "	0.0008 " —
0.0273 "	0.5 "	5 "	0.0262 "	0.0011 " —
0.0136 "	0.2 "	5 "	0.0132 "	0.0004 " —
0.0011 "	0.2 "	5 "	0.0009 "	0.0002 " —

The errors of both sets of experiments, those of Table I and those of Table II, are considerable, all lie in the same direction, and are indicative of too low registering of the action of the nitrate, since of the complete decomposition of the nitrate there can be no reasonable doubt in view of the proved behavior of the manganese salt toward small amounts of nitrates. To us it seemed probable that the explanation of these results was to be sought in the failure of the titration in alkaline solution to indicate completely all the final products of the action of the nitrate. The formation, even in small amounts, of compounds of nitric oxid with iodin analogous to those which we know to be formed with bromin and chlorin, or the partial reoxidation of the nitric oxids by the action of iodin with the aid of water, an action which we recognize as possible under certain conditions of dilution, would account satisfactorily for the deficiency in the results of titration effected in alkaline solution. Upon this presumption the simple and obvious modification of titrating in acid solution should correct the error.

Accordingly in the following series of experiments the plan of collecting the halogen and titrating in alkaline solution was abandoned, and since the addition of an iodid to the retort was no longer essential this practice was discontinued. The products of the action of the nitrate upon the manganese mixture—chlorin, nitric oxid and perhaps nitrosyl chlorid,—were received directly in potassium iodid, and the iodin set free was titrated by sodium thiosulphate, itself standardized against iodin of known value with respect to a standard solution of decinormal arsenious oxid.

With the abandonment of the plan of putting the [illegible] nite into the receiver the tendency of the [illegible] to pass [illegible] the second receiver is augmented and the possibility [illegible] rubber stopper of the receiver becomes correspondingly [illegible] We modified the apparatus, therefore, so that [illegible] occur where by any possibility rubber corrode [illegible] the free halogen. In place of the ordinary retort we [illegible] of apparatus made use of [illegible] distillation of hydrochloric acid under the action [illegible] petroleum and fitted [illegible] was called a Varrentrapp [illegible] Will-Anschütz [illegible] which was drawn out so that it might [illegible] inlet tube of the second receiver [illegible] Will-Anschütz [illegible] tion flask [illegible] and held [illegible] third receiver [illegible] to apparatus proper [illegible] [illegible] receiver [illegible] immediately after [illegible]

suitable time had elapsed for the removal of air heat was applied to the retort and the distillation was continued until nearly all the liquid had passed over. Finally the contents of the receivers were united, the washing of the bulbs was effected easily and expeditiously by passing the wash-water directly through retort and receiver (the introduction of the manganese chlorid into the distillate being not at all prejudical to the accuracy of the titration), and the estimation of free iodin made by sodium thiosulphate as described. The results of the experiments conducted in this manner are given in Table III.

These results are fairly satisfactory. The mean error of the entire series is practically nothing. The manipulation is easy and rapid.

In brief, the process which gives us these results consists in the distillation of the mixture of the nitrate with a saturated solution of crystallized manganous chlorid in strong hydrochloric acid in an atmosphere of carbon dioxid, the passage of the products of action into potassium iodid, and the titration of the liberated iodin by sodium thiosulphate. It is important to take precautions to prevent the contact of the free halogen with rubber stoppers or connectors, and any apparatus, suitable for ordinary quantitative distillation and absorption, which meets this condition will probably answer the requirements of the process. Our own preference is for the apparatus described and figured.

Table III.

KNO_3 taken.	$MnCl_2$ mixture.	KNO_3 found.	Error in terms of KNO_3.	Error in terms of HNO_3.
0.2038 gm.	20 cc.	0.2047 gm.	0.0009 gm.	0.0005 gm.
0.2053 "	20 "	0.2057 "	0.0004 "	0.0003 "
0.1032 "	10 "	0.1035 "	0.0003 "	0.0002 "
0.1017 "	10 "	0.1004 "	0.0013 "	0.0008 "
0.1049 "	10 "	0.1049 "	0.0000 "	0.0000 "
0.1027 "	10 "	0.1023 "	0.0004 "	0.0003 "
0.0524 "	10 "	0.0526 "	0.0002 "	0.0001 "
0.0513 "	10 "	0.0512 "	0.0001 "	0.0001 "
0.0354 "	10 "	0.0350 "	0.0004 "	0.0003 "
0.0232 "	10 "	0.0230 "	0.0002 "	0.0001 "
0.0107 "	5 "	0.0106 "	0.0004 "	0.0001 "
0.0127 "	5 "	0.0130 "	0.0003 "	0.0002 "
0.0145 "	5 "	0.0143 "	0.0002 "	0.0001 "
0.0053 "	5 "	0.0052 "	0.0001 "	0.0001 "
0.0043 "	5 "	0.0047 "	0.0004 "	0.0003 "
0.0014 "	5 "	0.0018 "	0.0004 "	0.0003 "
0.0000 "	5 "	0.0000 "	0.0000 "	0.0000 "

The titration should be completed as soon as may be after admitting air to the distillate in order that traces of dissolved nitric oxid may not be reoxidized and again react upon the iodid present to liberate more iodin.

CAN ARSENIC BE QUANTITATIVELY VOLATILIZED AS ARSENIC HYDRID?*

By F. W. Schmidt.

The question whether arsenic can be quantitatively volatilized as arseniuretted hydrogen has often been discussed. It was natural to utilize the beautiful reaction for quantitative determinations in which arseniuretted hydrogen in contact with a dilute solution of silver is transformed into arsenious acid and metallic silver. But in by far the most cases the researches undertaken for this purpose have led to no result, since it was not found practicable to convert entirely either arsenic or antimony into volatile hydrogen compounds, though we find in literature indications that this has been effected in certain cases, especially when the quantities of arsenic were only small. Still no decisive conclusion was reached, and Fresenius pronounces a severe condemnation (*Lehrbuch der Quantitativen Analyse*, **1**, 641), on all gravimetric processess founded upon the volatility of arseniuretted and antimoniuretted hydrogen.

If I felt induced to resume experiments in this direction it was because an observation had shown that the entire arsenic present in commercial zinc-powder could be volatilized as arseniuretted hydrogen on treatment with hydrochloric acid. The following method was therefore adopted.

In the first place the accuracy of the above mentioned observation had to be quantitatively confirmed. 10 gms. of commercial zinc-powder were carefully dissolved in concentrated nitric acid (concentrated acid was used to prevent the volatilization of traces of arsenic), the nitric acid present was expelled by evaporating down the solution obtained on the water-bath along with concentrated hydrochloric acid, and after reducing the arsenic acid by means of ferrous chlorid the arsenic was distilled over as $AsCl_3$ according to E. Fisher's process. The arsenic was then determined in the distillate as trisulphid in the ordinary manner, whence it appeared that the commercial zinc-powder contained 0.04 per cent. of metallic arsenic. As a check, a second

*Chem. News from Zeit. Anorganische Chemie.

portion of 10 gms. of the zinc-powder was submitted to the same operation, the $AsCl_3$ driven over on the addition of an excess of ferrous chlorid, the distillate supersaturated with sodium bicarbonate, and the arsenic titrated by means of decinormal solution of iodin; the 1.16 cc. of the solution consumed represent in the same manner 0.04 per cent. of metallic arsenic.

As the proportion of arsenic in the zinc powder was thus established, I could proceed to the determination of the arsenic in the form of arseniuretted hydrogen. The apparatus used for this purpose consisted of a round flask of the capacity of 200 cc., fitted with a dropping funnel and a gas-delivery tube leading to three absorption vessels each holding 100 cc. The flask is placed upon a water-bath so that the reaction may be assisted by heat. The distance of the first absorption vessel from the round flask is at least 20 cc., so that the liquid in the former may not become heated. The first absorption vessel is half filled with a solution of silver of the concentration 1 : 50; the second contains silver solution of the concentration 1 : 10, and the third contains bromo-hydrochloric acid. Ten grams of the commercial zinc-powder were weighed into the round flask; the substance was moistened through with water, the apparatus is connected together, and hydrochloric acid (1 vol. concentrated acid diluted with 1 vol. water), is gradually introduced by the dropping funnel. The gas liberated at once deposited black metallic silver in the first absorption vessel. As soon as the escape of gas became sluggish the flame was lighted beneath the water-bath and when the zinc-powder was fully dissolved a slow current of hydrogen previously washed in silver solution (1 : 10), and consequently free from arsenic, was passed through the apparatus for about half an hour so as to sweep the last traces of arseniuretted hydrogen out of the round flask. The contents of the third absorption vessel, and the liquid in the round flask, were found on careful examination utterly free from arsenic; all the arsenic, therefore, as in the first observation, had been volatilized as a hydrogen compound, and at the same time the transformation of the arseniuretted hydrogen with the silver solution was completed in the second absorption vessel, so that the third contained not a trace of arsenic. From the contents of the first and second absorption vessel, the excess of silver was separated by means of sodium chlorid, and the arsenic in the filtrate from the

silver chlorid, after an addition of sodium bicarbonate, was titrated with decinormal solution of iodin. There were again used, until a blue color appeared, 1.16 cc. of the standard solution corresponding to 0.04 per cent. of metallic arsenic in the commercial zinc-powder.

This result rendered it very probable that the complete volatilization of the arsenic from zinc-powder in the state of arseniuretted hydrogen depends on the presence of the arsenic in the zinc-powder as a zinc arsenid, or else in an exceedingly finely divided metallic state which energetically assists the quantitative conversion of the arsenic into its hydrogen compound. A quantitative volatilization must therefore be attainable also in other cases if the arsenic is converted into a state analogous to combination or to fine metallic sub-division.

To decide the correctness of this assumption there were introduced into the round flask of the apparatus described above, in addition to 30 gms. of pulverized zinc (zinc can be readily pulverized at 205°), 20 cc. of a 1 per cent. solution of arsenic containing 0.119 gm. of arsentrioxid. (One gm. of commercial arsenious acid was dissolved in 100 cc. of water; 20 cc. of this solution consumed 40.2 cc. decinormal iodin, corresponding to 0.199 gm. pure arsentrioxid). The first absorption vessel was again charged with solution of silver 1 : 50, the second and third with solution silver at 1 : 10. After the apparatus was put together, hydrochloric acid (1 : 1) was again allowed to enter by means of the dropping funnel as before, heat was applied until the zinc was entirely dissolved, and finally hydrogen free from arsenic was passed through the apparatus. The titration of the contents of the absorption vessels (after precipitating the excess of silver by means of sodium chlorid, etc.) used only 38.4 cc. decinormal solution of iodin, which corresponds to 0.190 gm. arsenious acid; hence nearly 5 per cent. of the original quantity of arsenic had remained in the round flask,—a result which confirms those formerly obtained by other authors.

Now came the decisive experiment, which was effected in the same manner with 20 cc. of the 1 per cent. solution of arsenic and 30 gms. of powdered zinc. When after heating for one hour the development of arsenic became sluggish, there was added to the contents of the round flask through the dropping-funnel an agent

calculated to produce a state of the arsenic analogous to "combination or fine metallic distribution," *i. e.*, a hydrochloric solution of stannous chlorid (obtained by dissolving non-arseniferous tin foil in concentrated hydrochloric acid).

At the moment when this solution was dropped into the round flask there appeared at once a turbidity and then a dark precipitation. Both the turbidity and the precipitate disappeared in a few minutes after a little platinum chlorid had been added to re-animate the development of hydrogen, and the liquid resumed its former appearance. The application of heat was still continued for about 15 minutes, and a current of hydrogen free from arsenic was then passed through the apparatus for about the same time. The titration of the contents of the absorption vessels then showed exactly 0.119 gm. of arsenious acid, since 40.2 cc. decinormal iodin solution were required for its conversion into arsenic acid. The residue in the round flask, on careful examination showed no trace of an arsenical reaction.

Hence it follows with great probability that the above assumption is correct, though it is conceivable that the stannous chlorid in addition to its property of precipitating arsenic in a very finely-divided metallic condition, has also a catalytic action, since stannous chloride is continually regenerated in the liquid. Its *modus operandi* is further explained by the following observations. After proceeding as usual, and as the zinc in the round flask was chiefly dissolved, solution of stannous chloride containing 1 or 2 gms. of metallic tin was allowed to flow slowly in through the dropping funnel. The tin was by degrees rather quickly separated out as a spongy mass, which dissolved only slowly on the addition of concentrated hydrochloric acid, but could be easily dissolved with a brisk escape of hydrogen on the addition of a little platinum chlorid. These spongy masses were taken out of the liquid for closer examination and washed in distilled water. It was then found that they had taken up the main part of the arsenic present in the liquid which retained only traces. Whether in this case the arsenic as separated really combines with the tin as tin arsenid, or if the arsenic remains in the spongy tin in a state of fine metallic division, must be left undecided.

In a check experiment the following conditions were observed. As working with the apparatus above described offers the incon-

venience that the addition of liquids into the hot round fl through the dropping funnel can be effected only with the gre caution, in order to avoid a reflux occasioned by the [illegible] cooling, there was inserted after the round flask [illegible] 300 cc. of materials, a Woulf's bottle, holding [illegible] the gas troductory tube of which was provided with a Bunsen valve o glass ball valve. Thus a reflux was rendered impossible and was no longer necessary to observe the working of the apparat The Woulf's bottle was now connected with three receivers e of the capacity of 100 cc., all contained silver solution [illegible] the Woulf's bottle as much as corresponded to the arsenic used the experiment

The precaution was also employed that all the liquids should forced into the round flask by a pressure of hydrogen, when any ascent of gas bubbles in the dropping flask was at once cluded

Since the zinc used not the same as that used in the [illegible] periments which had all been consumed was found [illegible] amination to contain a minimum trace of zinc this trace was determined in the apparatus [illegible] grms of the zinc were found contain [illegible] per cent of arsenic corresponding [illegible] decinormal solution of [illegible] which was [illegible] the contents of the receivers. It therefore [illegible] per cent solution of [illegible] which required [illegible] per cent of decinormal solution of [illegible] were [illegible] the paratus is arsenic hydrid by means of [illegible] tion of the contents of the receivers [illegible] of silver, [illegible] liquid. This was [illegible] summed [illegible] decinormal solution. [illegible] was monstrated

Further experiments [illegible] a solution of silver [illegible] concentration is only [illegible]

black silver antimonid, upon which behavior the separation of both elements may possibly be based.

This profound difference in the behavior of both hydrogen compounds with dilute solutions of silver is also theoretically interesting. If we reflect that in the oxygen compounds of the trivalent elements, N, P, As, Sb, consequently in N_2O_3, P_2O_3, As_2O_3, Sb_2O_3, the acid character continually decreases, and that with higher atomic weights basic characters become more perceptible, and that in the corresponding hydrogen compounds, NH_3, PH_3, AsH_3, SbH_3, the behavior is exactly the reverse, we are inclined to ascribe to antimony hydride faintly acid properties which come clearly into evidence in their action upon dilute silver solutions. For the recognition of antimony hydrid as a feeble acid—feebler than hydrogen sulfid—we have the testimony of the occurrence in nature of silver antimonid, whilst silver arsenid is known neither chemically nor as a mineral.

The above described method is a simple means for the determination of arsenic, and is the more important in toxicology, as in forensic inquiries arsenic is almost exclusively recognized by the Marsh test.

NEW METHODS OF ESTIMATING CHROMIUM IN FERRO-CHROMIUM AND STEEL.*

By John Clark, Ph.D.

FERRO-CHROMIUM.

On account of its technical importance the estimation of chromium in ferro-chromium has engaged the attention of a considerable number of chemists, but the processes hitherto published are for the most part very tedious. This is to a large extent due to the difficulty which is experienced in getting the whole of the chromium into solution, as alloys rich in chromium are only partially soluble in nitric, sulfuric, or hydrochloric acids, or even aqua regia.

H. N. Warren, it is true (*Chem. News*, **65**, 186), states that ferro-chromium is readily dissolved by heating with strong sulfuric acid, but I have not succeeded in completely dissolving in this way the alloys which I have had occasion to test, the best result obtained after heating with H_2SO_4 for a day giving 8.9 per cent. of insoluble chromium, and as they frequently contain alumi-

*J. Soc. Chem. Ind., **11**, 501.

num his method of estimating the chromium by weighing the precipitates of oxids of chromium and iron, and deducting the iron is, in my opinion, scarcely entitled to be called accurate. According to R. Schöffel (*Ber. Deutsch. Chem.* 1879, 1863) even direct fusion with carbonate of soda and nitrate of potash is of no use, and he therefore recommends that the greater portion of the iron of the ferro-chromium should be dissolved out with the double chlorid of copper and sodium or ammonium, and the residue fused with carbonate of soda and nitrate of potash, but he admits that this process is not suitable for alloys containing more than 8 per cent. of chromium.

A. Ziegler states that ferro-chromium can be dissolved by fusion with a large excess of bisulfate of potash or soda, but he recommends (*Ding.* **279,** 163) that the ferro-chromium should be fused with a mixture of 6 parts of caustic soda and 3 of nitrate of potash and the chromium in the solution twice precipitated with ammonia after evaporation to dryness with hydrochloric acid to render the silica insoluble. In addition to this, the portion insoluble in water is dissolved in hydrochloric acid, and the oxid of iron tested for chromium.

In 1871 (*Chem. News*, **24,** 286 and 304) I published a new method of estimating chromium in chrome iron ore, depending on the oxidation of the chromium by means of a mixture of caustic soda and magnesia, and subsequent titration of the chromic acid. In 1877, or fully five years afterwards, this process was reproduced by A. Christomanos as his own in a paper read before the German Chemical Society (*Ber. Deutsch. Chem.* **10,** 16). I did not observe this publication at the time and would have taken no notice of it now, but I find that in Roscoe and Schorlemmer's Treatise on Chemistry (**2,** Part 2, p. 183), Christomanos is referred to in a foot-note as the author of the process, and I therefore take this opportunity of pointing out my claim to priority. This process is very suitable for ores or oxid of iron precipitates, as the oxid of chromium is readily converted into chromic acid at the temperature of a Bunsen flame, but on applying it to poor ferro-chromium under the same conditions so little oxidation took place that I concluded it was necessary to oxidize the chromium before it could be converted into chromic acid by soda and magnesia. Unfortunately, ferro-chromium is only partially oxidized

in the muffle or over a blow-pipe, and even when heated in pure oxygen by means of a gas combustion furnace oxidation takes place very slowly. I found, however, on repeating my experiments with rich alloys of chromium, that when the temperature was lowered to a point at which it seemed scarcely possible that any action could take place the ferro-chromium, even when in coarse powder, was readily and rapidly oxidized by the soda and magnesia without the use of an oxidizing agent such as chlorate or nitrate of potash, any excess of which would interfere with the subsequent titration of the chromium.

Magnesia and Soda Process.—One gram of the finely pulverized ferro-chromium is intimately mixed in a platinum crucible with 5 gms. of magnesia mixture, consisting of two parts of freshly calcined magnesia, and three parts of finely pulverized hydrate of sodium, and the crucible is placed over a low Bunsen flame in such a manner that only the point of the flame touches the bottom of the crucible. Oxidation begins almost immediately, and takes place so rapidly that the contents of the crucible actually glow for several minutes. After heating at this temperature for about half an hour without stirring, the flame is raised and the bottom of the crucible maintained at a dull red heat for another half hour. The contents, which consist of an adherent powder, are then washed into a porcelain basin and boiled for some minutes to dissolve out the chromate, which is either pure yellow or slightly green in color if manganese is present. To decompose the manganate peroxid of hydrogen is added drop by drop till there is no further change of color, and after boiling for a few minutes to remove any excess of peroxid of hydrogen the solution is filtered, acidified with sulfuric acid, and the chromium estimated by adding an excess of ferrous ammonium sulfate, and titrating the unoxidized iron with a standard solution of bichromate of potash. Although the bulk of the chromium is rendered soluble in the first fusion, a little always escapes oxidation. To extract this the insoluble portion on the filter is ignited, ground in an agate mortar, and again fused with about twice its bulk of magnesia mixture for about half an hour, and the chromic acid is estimated as before. The insoluble portion is now washed into a beaker or basin, and the bulk of the magnesia is removed by adding dilute sulfuric acid till the reaction is neutral. The oxid of iron is then filtered off and again

fused with magnesia mixture, when the last traces of chromium will be obtained.

Example.

	Gms. Found.	Per Cent.
1st fusion	0.5491	54.91
2d "	0.0320	3.20
3d "	0.0096	0.96
4th "	.	. .
Total	0.5907	59.07

Lime and Soda Process.—Rich ferro-chromium can also be oxidized by heating the finely pulverized alloy in the manner already described with five times its weight of lime (CaO) and sodium hydrate in equal proportion. In this case it is advisable before filtering to add about 2 gms. of bicarbonate of sodium to convert the lime into carbonate, but in other respects the process is the same. As a rule, however, at least four fusions are needed to extract the whole of the chromium.

Calcium Hydrate Process.—Although alloys of chromium are difficult to oxidize when heated alone either in air or oxygen, they are readily converted into oxid at high temperatures in presence of calcium hydrate, and this fact can be utilized for the estimation of the chromium as follows :

One gm. of the finely pulverized ferro-chromium is mixed with three times its weight of calcium hydrate and heated in a platinum, nickel or porcelain crucible in a muffle or over the blow-pipe for about half an hour when oxidation is practically complete. The action takes place most rapidly in platinum or nickel, but the platinum is strongly acted upon, and the nickel usually gives way after being used two or three times. It is therefore more economical to use a porcelain vessel. The contents of the crucible consist of a green powder, which can easily be crushed with a glass rod and contains no chromate. The oxid of chromium thus formed may be converted into chromic acid by adding to the crucible 5 gms. of the magnesia and soda mixture above referred to, stirring with a rod and heating in the muffle or over a Bunsen for about an hour; but when the ferro-chromium is employed in coarse powder it is advisable to grind the lime fusion before the addition of the magnesia mixture. The contents of the crucible, which

seem to have little or no action on the porcelain, are boiled with water and a little peroxid of hydrogen, filtered after the addition of about 3 gms. of bicarbonate of sodium, and the chromic acid titrated in the manner already described. As a small quantity of the chromium usually escapes oxidation, the insoluble portion is again heated with about its own bulk of the magnesia and soda mixture for about half an hour, and the chromate estimated as before. The insoluble portion should now be neutralized with dilute hydrochloric acid to remove the bulk of the lime and magnesia, and the residue subjected to a third fusion to ensure the extraction of the last trace of chromium.

Example.

	Nickel Crucible.		Porcelain Crucible.	
	Found.	Per Cent.	Found.	Per Cent.
1st fusion	0.5645	56.45	0.4904	49.04
2d "	0.2321	2.31	0.0673	6.73
3d "	0.0045	0.45	0.0323	3.23
4th "	. .	.	0.0025	0.25
Total	0.5921	59.21	0.5925	59.25

This process works well, and is more suitable for poor alloys of chromium than those which I have already described.

The oxid of chromium produced by heating 1 gm. of the ferro-chromium with hydrate of calcium may also be converted into chromic acid by heating with 4 gms. of carbonate of soda in the muffle, but, as a rule, a smaller yield of chromate is obtained in the first fusion and more fusions are required. In other respects the process is the same and the results equally correct.

Example.

	Cr Found. Gm.	Cr Per Cent.
1st fusion	0.4535	45.35
2d "	0.1064	10.64
3d "	0.0193	1.93
4th "	0.0083	0.83
5th "	0.0020	0.20
Total	0.5895	58.95

Sulfur Process.—The disintegration and oxidation of ferro-chromium can also be effected by means of sulfur instead of hydrate of calcium. For this purpose 1 gm. of the finely pulverized

alloy is placed in a porcelain boat and subjected for about [illegible] minutes to the action of sulfur vapor in a porcelain tube heated [illegible] an ordinary gas combustion furnace. As soon as the vapor comes in contact with the heated ferro-chromium a strong [illegible] takes place, the metal glows and swells up to several times its original bulk, and a little powder is apt to be carried away mechanically by the sulfur vapor and scintillates. The product, which is greyish black in color, is the form of a fine powder and consists essentially of Cr_2S_3 and FeS. The sulfid thus produced is carefully ground in an agate mortar, and may be [illegible] converted into chromate by heating over a Bunsen with eight times its weight of the magnesia and soda mixture already referred to. [illegible] may be converted into oxid by ignition in a porcelain crucible [illegible] with five times its weight of the mixture, and the chromate is titrated as already described after removing the magnesia.

Example.

	[illegible]	[illegible]	[illegible]	[illegible]
1st fusion	[illegible]	[illegible]	[illegible]	[illegible]
2d	[illegible]	[illegible]	[illegible]	[illegible]
3d	[illegible]	[illegible]	[illegible]	[illegible]
4th				
Total	[illegible]	[illegible]	[illegible]	[illegible]

The results obtained by this method are rather [illegible] than the other processes, but this is more apparent than real, [illegible] caused by the slight mechanical loss [illegible].

The ferro-chromium may also be completely converted into sulfid by heating with [illegible] sulfur [illegible] crucible over a Bunsen [illegible] the operation [illegible] takes place [illegible] the bulk of the [illegible] and mechanical [illegible].

[illegible] exposing the [illegible] process [illegible] this [illegible] over [illegible] chance of loss [illegible] heated [illegible]

sia and sodium hydrate either with or without previous roasting, and the chromium estimated as described. One gram ferro-chromium gave with this treatment:—

	Cr Found. Gm.	Cr Per Cent. Gm.
1st fusion	0.5789	57.89
2d "	0.0056	0.56
3d "	0.0018	0.18
4th "	. .	. .
Total	0.5863	58.63

STEEL.

On account of its greater solubility in acids, the estimation of chromium in steel is usually considered to be easier than in ferro-chromium, but I must confess it has given me more trouble. I have already indicated that poor alloys of chromium are very imperfectly oxidized when heated direct with sodium hydrate mixed with magnesia or lime, and the same holds good to a still greater extent with steel. Calcium hydrate works better, but the oxidation of the chromium seems to be prevented by the formation of a crust of oxid of iron; and when this method is used it is necessary to grind the lime fusion once or twice to expose a fresh surface. When this is done, fairly good results are obtained, but the sulfur and carbon bisulfid processes are by far the best. When steel turnings are exposed to the action of sulfur vapor, there is no indication of mechanical loss as in ferro-chromium, and the sulfid produced appears slightly fused. Sometimes it adheres to the porcelain, but it can generally be detached, in which case it is pulverized, then roasted in a porcelain crucible, and fused with four times its weight of the mixture of magnesia and sodium hydrate already referred to, and the chromium estimated as described.

When the sulfid adheres firmly to the porcelain, it is ignited in the boat itself till it can be detached and ground. Two fusions are generally sufficient for the extraction of the whole of the chromium.

Example.

Three grams of a steel received from Mr. R. A. Hadfield, of the Hecla Works, Sheffield, and said to contain 1.60 per cent. of chromium, gave the following results by this process:—

	Cr Found Gm	Cr Per cent	[illegible] Gm	[illegible] Per cent
1st fusion	[illegible]	[illegible]	[illegible]	[illegible]
2d "	[illegible]	[illegible]	[illegible]	[illegible]
3d "	[illegible]			
Total	[illegible]	[illegible]	[illegible]	[illegible]

Although the sulfur process works well the [illegible] method is, in my opinion, the best for steel. It is most [illegible] iently carried out by attaching a flask containing [illegible] to one end of the porcelain tube and a small condenser to the [illegible] and passing a gentle stream of CS_2 vapor over the heated steel about an hour. On the removal of the heat it will be [illegible] that the steel drillings have increased considerably in [illegible] and soft and porous, but they retain their original form. As the product has no tendency to adhere to the porcelain it can at once be transferred to a crucible and roasted. Oxidation takes place very rapidly, and in the course of about half an hour the substance is converted into a fine powder without stirring or grinding and may be at once heated with four times its weight of the mixture of magnesia and sodium hydrate and the chromate extracted and estimated as described.

Example.

Two grams of the steel from the Hecla Works treated in this way

	[illegible]	[illegible]
1st fusion	[illegible]	[illegible]
2d "	[illegible]	[illegible]
3d "		
Total	[illegible]	[illegible]

These methods [illegible] the [illegible] the [illegible] of course the [illegible] and treated as one.

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COPPER SULFATE AS A MATERIAL FOR STANDARDIZING SOLUTIONS.

BY EDWARD HART.

Since the paper by Croasdale and myself was published (see this Journal 4, 424) I have had considerable experience in the use of the method there detailed and find it to be extremely accurate. Several things remained to be proven which I intended to take up and press to a solution; but they have, in the meantime, been solved with a great deal of accurate and painstaking work by Prof. T. W. Richards in the course of his investigation on the atomic weight of copper.* The points to be solved were:

1. What is the exact ratio between Cu and SO_4 in copper sulfate?

Prof. Richards finds that the ratio between Cu and SO_4 is, neglecting the first series:†

	Cu	:	SO_4	
Second Series	25.450	:	38.436	mean 25.449 : 38.436
Third Series	25.448	:	38.436	

or

Cu	:	SO_4	=	Cu	:	SO_4
25.449	:	38.436	=	63.604‡	:	96.062

or

$$Cu : H_2SO_4 = 63.604 : (96.062 + 2.014\S) = 98.076$$

or

$$Cu : H_2SO_4 = 1 : 1.54197$$

2. How can we get copper sulfate pure, and absolutely normal or free from excess of acid?

*See especially his fourth paper, Proc. Amer. Acad. 26, 240.
†Ibid. 26, 260, second table. ‡ Ibid. 26, 293.
§ For H_2, see this JOURNAL 5, 55.

It is quite easy, as Prof. Richards* and Hampe* have shown, to prepare copper sulfate by adding to the solution a trace of potassium hydroxid, to precipitate bismuth and iron, and ammonium bromid to throw down silver. Richards† has also shown that methyl orange may be used as a test of neutrality, and that it is easy to detect a very minute excess of acid in this way.

When electrolytic copper is dissolved in hot concentrated sulfuric acid and the resulting hard cake dissolved in water, a black residue of copper sulfid remains, evidently formed by the reduction of sulfur dioxid by the metallic copper. It is possible that this reduction of sulfur may remove some of the foreign metals present; the examination of this point I must, however, postpone for the present. All the copper sulfate used was prepared in this way from electrolytic copper, and was very pure.

In our first paper the addition of sodium or potassium sulfate was recommended for the purpose of increasing the [illegible] of the solution. This addition seems, however, to be unnecessary, and I find that potassium sulfate is quite inadmissible, as [illegible] insoluble sulfates are formed.

The sulfuric acid obtained from the copper sulfate [illegible] used for standardizing another solution, and since it was [illegible] portant that the keeping qualities of the solution should be good, I concluded to use decinormal sulfuric acid, using an [illegible] sodium carbonate solution as intermediary.

Phenol phthalein was chosen as the indicator, and the [illegible] used containing a little water and a trace of the indicator [illegible] boiled for half an hour to be sure that nothing alkaline [illegible] go into solution during boiling. In this way I have [illegible] make up in a short time by the method of Mixer [illegible] and with the greatest exactitude seven or eight liters [illegible] normal sulfuric acid enough to serve for a long time as standard for alkalimetric work. The strength after [illegible] was found to be such that [illegible]

I have made no attempt to compare the sulfuric acid obtained from the copper sulfate with sodium carbonate by weight since this has already been done with the greatest exactitude by Prof. Richards in his fourth paper on the atomic weight of copper already cited.

A committee of the Association of Official Agricultural Chemists have compared our method with others and speak well of it. I doubt whether their report adds to the evidence in either direction, however, since their ultimate standard was a solution of hydrochloric acid the strength of which was determined by precipitation with silver nitrate. Every chemist knows, however, that it is an easy matter to make an error of half a milligram in any method involving a precipitation and the transfer of a precipitate; Croasdales results* and those of Richards† show that the error involved is much less when copper is determined by the battery method, and that we can probably determine copper more accurately than any other element, consequently that our method should be taken as the standard and others referred to it.

A NEW METHOD FOR THE DETERMINATION OF SODA IN SOAP, TOGETHER WITH A FEW NOTES ON METHODS GENERALLY EMPLOYED.

By Wilson H. Low, Chemical Director of N. K. Fairbank & Co., Chicago, Ill.

In the ordinary method of soap analysis, the sample is dissolved in neutral alcohol and filtered from any insoluble residue, which is washed, dried and weighed and further examined if necessary. The soap is in the alcoholic solution together with other matters soluble in aqueous alcohol, such as a small amount of carbonate of soda, the whole or almost the whole of the chlorid and sometimes other matters of mineral or vegetable origin. A little phenol-phthalein is added to the solution to serve as an indicator and if alkaline, acid is added to neutralize and the amount used calculated to sodium hydroxid, and if acid, alkali is

* This Journal 5, 140.
† Proc. Amer. Acad. 26, 262.

added and the amount calculated to fatty acid. Neither of these titrations expresses the exact truth but they are the ones generally employed for the purpose. The main errors are due to the fact that sodium carbonate is soluble to a slight extent in [illegible]ary alcohol and gives an alkaline reaction with phenolphthalein, this being estimated as caustic, and also the combining weight of the free fatty acid or acids is rarely known very closely [illegible] by no means necessarily the same as the mean combining weight of the mixed fatty acids in soap. In fact the free fatty acid has generally a very different combining weight. This latter source of error is usually greater than the estimation of caustic as the combining weights of the fatty acids are so high it is a difficult thing to estimate exactly in small quantities. It is my [illegible] unless the free fatty acids are present in considerable quantity to disregard them entirely. This does not apply to the [illegible] and unsaponifiable matter, which are determined in a [illegible] manner.

After the above operations the soap is present as a [illegible] compound together with the other matters soluble [illegible]. The solution is evaporated to dryness to expel the [illegible] then dissolved in hot water and an excess of standard [illegible] in to set free the fatty acids. These are separated from the [illegible] solution in any suitable manner and the latter shaken [illegible] with neutral ether to remove any fatty acids from the [illegible] and the ether solution evaporated to dryness and the [illegible] weighed and added to the weight of the main [illegible] fatty acids.

The ether is evaporated from the acid solution and the [illegible] cooling, the excess of acid used is estimated by back titration with [illegible] using methyl orange as indicator. The [illegible] salt or chloride is next found by titration of the neutral [illegible] [illegible]

The [illegible] general idea of the [illegible] It has [illegible] to go into [illegible] that may [illegible] so well [illegible] as I know [illegible] considerable [illegible] some commercial samples [illegible] [illegible] estimation is the only way to [illegible] [illegible]

As can be seen by the scheme outlined, several operations will be performed and considerable time consumed before the soda combined with the fatty anhydrides as soap will be known. As it is often a matter of importance to determine this in a short time some quicker method was looked for. Direct ignition of the soap and titration of the residue is only applicable to a pure soap containing no free or carbonated alkali; further, another portion of the soap must be weighed out if the other constituents are wanted.

Allen (**2**, 260) states that the combined soda in a soap may be determined in aqueous solution by adding standard acid gradually till methyl orange indicates a slight excess. My own experience confirms this, if it is done carefully and the solution is not too hot. The tendency is to get in too much acid as the separated fatty acids give the liquid a milky appearance which somewhat masks the end reaction.

Blue lacmoid solution may be used in place of methyl orange but possesses no particular advantage in aqueous solution. In any case the method can only be used when there is no free caustic or carbonated alkali.

In his notes on the various indicators and their behavior in different solutions under changed conditions, R. T. Thomson states (*Chem. News*, **52**, 18, July, 1885) that "*red lacmoid paper* shows almost instantaneously even a slight alkalinity, in the strongest alcohol, and if the alcohol containing a trace of alkali be colored blue with lacmoid solution, one drop of normal acid will change the color immediately." This statement has been confirmed by the writer, and also if 100 to 200 cc. of neutral alcohol be colored slightly blue with a lacmoid solution, one drop of normal acid will give a strong bright red coloration, which change from blue to red is very sharp.

Thomson further states in regard to methyl orange, "100 cc. of alcohol requires at least 0.5 cc. of normal acid to effect even a slight change in color. Several cubic centimeters are necessary to bring out the full color. The end reaction is indistinct. When diluted with five or six times its volume of water, alcohol has very little effect on methyl orange and its effect may be disregarded.

It is thus seen that while blue lacmoid solution and methyl orange behave the same in aqueous solution, in alcoholic solution methyl orange is useless.

From the fact that blue lacmoid solution was affected very little, if any, by ordinary insoluble fatty acids when separated in an aqueous solution and also that it was a good indicator of mineral acids in alcoholic solution, it was hoped that the fatty acids in alcoholic solution would have little effect on the indicator. This was found to be the case and is the foundation of the present process.

When blue lacmoid solution is added to a boiling hot neutral solution of soap in ordinary alcohol, it gives the liquid a bluish tint and of about the same shade as if no soap were present. Now on adding a drop of normal acid little, if any, change will occur and the blue tint will remain on further addition of acid till within a few cubic centimeters of the end point, when the indicator begins to lose its color and appears like fine black particles mixed with clear water. A little more acid causes the indicator to give a slight reddish tint to the liquid. It is not a pure red and is not like the red given by the final reaction. When this point is reached the acid should be added slowly or drop by drop till the indicator gives the liquid a pure bright red coloration. This point is easily distinguished from the previous reddish tint and further addition of acid causes no change in it. In a colorless soap solution the change is well marked and even in solutions of soap of themselves a yellow or brown color the end reaction is apparent by the change to a pure bright color something like the clearing up of the solution. The amount of indicator to use depends on the depth of color of the original soap solution. Enough must be used so that its change of color will easily overcome any given by the soap itself. In turbid soap solutions caused by insoluble matter in suspension the clear bright red color cannot be seen but the end point of the reaction is well marked by a decided change in the color of the liquid that by the addition of a drop or two of acid. A little practice will make it clear when the end reaction occurs. The one thing to emphasize is to [illegible] but to [illegible] till the change is [illegible] addition of acid leaves the

liquid of the same tint. If this is attended to, with some practice the soda combined with the fatty anhydrides as soap can be titrated accurately.

In a mixtre of soap and carbonated alkali the soda in each can be determined without filtration and more accurately than when the carbonate is removed by filtration and subsequently titrated or weighed by itself. The source of error in this last method lies in the fact that sodium carbonate is somewhat soluble in ordinary or aqueous alcohol and passes into the filtrate with the soap and in the ordinary analyses finally turns up and is estimated as soda combined as soap. This error is greater the more alcohol there is used and the more water it contains. If little alcohol be used some soap is apt to be left with the sodium carbonate, as in washing powders the mixture of soap and soda ash is so intimate that complete solution of the soap does not take place immediately and sometimes long soaking in warm alcohol is the best way to effect solution.

In the method indicated below the above objections do not enter and the total sodium carbonate is estimated as such and the soda in the soap determined as well.

Weigh out a few grams of the soap into a flask and treat with 50 to 100 cubic centimeters of neutral alcohol. Heat to boiling to effect the solution of most of the soap at least and then run in enough normal hydrochloric acid to more than decompose the carbonate present. Heat to boiling and continue the boiling five to ten minutes to completely expel all the carbon dioxid. A good strong ebullition is necessary to do this. Now add some phenol-phthaleïn to serve as indicator and titrate back with sodium hydroxid to pink color with the indicator. In the first operation all the carbonate was decomposed and part of the soap, so that free fatty acids were present; in the second operation the alkali was restored to the fatty acids leaving a neutral soap solution and the difference between the total amount of hydrochloric acid added, and the amount of hydrochloric acid equivalent to the sodium hydroxid used in back titration is a measure of the carbonated alkali. The soda in the soap is now estimated as given above by means of standard hydrochloric acid and blue lacmoid solution as indicator. If the combining weight of the

fatty anhydrides is known they may be calculated from the soda found as soap; but usually they are not known accurately and have to be estimated by weight. A good method of doing this is to add alkali to the above alcoholic solution till the free fatty acids are again made into soap and then evaporate off the alcohol on a water or steam bath. Treat the residue with hot water and set free the fatty acids with a slight excess of standard hydrochloric acid. As soon as the acids have run clear, cool the solution, with constant agitation to break up the solidified fatty acids into pieces about the size of a pin-head. When perfectly cold the fatty acids are removed from the solution of neutral salts by filtration through paper or a Gooch crucible. They are washed somewhat with cold water to remove soluble salts and if they are cold there is no tendency to pass through the paper. A Gooch crucible with a gentle suction is much the best for this purpose. Draw air through a short time after the washing to get rid of all the water possible and then placing the filter over a weighed flask, run hot alcohol (the stronger the better) upon the fatty acids. They dissolve and pass into the flask. Wash the filter well and to the filtrate add a small amount of phenol phthalein and titrate to neutrality or slight alkalinity with normal or half normal *alcoholic* soda free from carbonate. We now have present in solution a neutral soap made from the original fatty acids which has not undergone heating or unnecessary exposure to air and they have not lost weight by becoming anhydrides as sometimes happens on drying fatty acids in an oven. There was glycerin present and all that is wanted to determine the corresponding weight of the anhydrides directly is to evaporate the soap solution to dryness and weigh. The amount of soda present is known and the difference is fatty anhydrides. This method is more accurate than weighing the fatty acids and multiplying by [illegible] is certainly less liable to error. If there were any soluble fatty acids in the original soap they would have passed into the filtrate with the insoluble acids and [illegible] then the liquid is shaken with ether, the ether solution mixed with a little alcohol and phenol phthalein added, and the solution run to neutrality. The soap formed is evaporated to dryness and weighed as before. No assumption has to be made as to the fatty acids or acids present

The experiments showing the applicability of blue lacmoid solution as an indicator for titrating combined alkali in an alcoholic soap solution are given below. Solutions used:

Hydrochloric acid solution.—1 cc.=0.024938 gms. soda =0.042608 gms. sodium carbonate. This was standardized by sodium carbonate, using phenol-phthaleïn as indicator in boiling solution. The sodium carbonate used contained 99.90% sodium carbonate as calculated from a determination of carbon dioxid.

Sodium hydroxid solution (freed from carbonate, etc., by means of Millon's base)—1 cc.=0.6200 cc. hydrochloric acid solution, using phenol-phthaleïn as indicator in cold or boiling solution. 1 cc.=0.6217 cc. hydrochloric acid solution with methyl orange in cold aqueous solution. 1 cc.=0.6219 cc. hydrochloric acid solution with blue lacmoid in hot alcoholic solution. These values are for running to decided alkaline reaction.

Burette readings were all corrected for calibration errors and at least three minutes drainage allowed. In all the following tests an unknown quantity of fatty acids was taken and made into soap by running in sodium hydroxid solution to just alkaline reaction to phenol-phthaleïn, the titration being in boiling hot alcoholic solution. The quantity of sodium hydroxid run in was not noticed till after the titration with acid, so that it should be no guide as to how much acid would be needed; also, in running in the acid, the burette was not watched, and every care was taken that the result should be wholly unaffected by any previous knowledge of quantities.

The results are expressed in terms of the hydrochloric acid solution as being the simplest way of comparison.

Experiment No. 1. About 5 gms. of stearic acid taken, dissolved in 100 to 150 cc. of neutral alcohol and heated to boiling. Made into soap by adding standard sodium hydroxid solution till just alkaline to phenol-phthaleïn. We now have practically a neutral soap solution and the soda combined as soap is found by titrating with hydrochloric acid, using blue lacmoid as indicator.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	35.23 cc.	35.22 cc.	21.90 cc.
HCl "	21.98 "	21.90 "	21.90 "

The exact amount of soda used was found.

Experiment No. 2. About 1 gm. of stearic acid taken.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	7.71 cc.	7.70 cc.	4.79 cc.
HCl "	4.90 "	4.87 "	4.87 "

Difference, 0.08 cc.

Experiment No. 3. About 2 gms. of palmitic acid taken and treated in the same way.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	14.57 cc.	14.57 cc.	9.06 cc.
HCl "	9.08 "	9.02 "	9.02 "

Difference, 0.04 cc.

Experiment No. 4. About 2 gms. of a dark rosin taken.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	13.48 cc.	13.47 cc.	8.38 cc.
HCl "	22 to 30.4 "	8.39 "	8.39 "

Difference, 0.01 cc.

Experiment No. 5. About 2.5 gms. of fatty acids from bleached soap from cotton-seed stock.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	17.39 cc.	17.40 cc.	10.82 cc.
HCl "	10.93 "	10.86 "	10.86 "

Difference, 0.04 cc.

Experiment No. 6. Fatty acids from a brown cotton-seed soap giving as dark an alcoholic solution as is usually met with.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	24.81 cc.	24.82 cc.	15.44 cc.
HCl "	15.50 "	15.43 "	15.43 "

Difference, 0.01 cc.

The exact amount of soda was found.

This result is particularly satisfactory as the alcoholic solution is of quite a strong brown color, and masks the indication with phenol-phthalein to some extent. The end point with lacmoid was decided, and the marked change in the appearance of the liquid easily recognized. It was not the bright, clear red as with a coloress soap solution but the decided change in color of tint marked the end reaction clearly.

Experiment No. 7. Some of the same lot of fatty acids used in No. 6 was taken and made into soap as usual and then a known amount of sodium carbonate added by putting in a measured quantity of solution.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	19.40 cc.	19.42 cc.	12.08 cc.
	(This saponifies the fatty acids.)		
HCl used	12.30 cc.	12.23 cc.	12.23 cc.
	(More than enough to decompose the sodium carbonate.)		

The solution was boiled about ten minutes (best done in an

Erlenmeyer flask) to expel all carbon dioxid, and then the alkali restored to the fatty acids by sodium hydroxid solution.

	Burette reading.	Corrected reading.	Equivalent in HCl sol.
NaOH used	19.42 to 22.22 cc.	2.80 cc.	1.74 cc.*
HCl "		12.23 minus 1.74 cc.	10.49 cc.†
The sodium carbonate added was equivalent to			10.46 cc.
		Difference, 0.03 cc.	

The soda combined as soap was next determined.

	Burette reading.	Corrected reading.	Equivalent of NaOH sol.
HCl used	12.20 cc.	12.13 cc.	12.08 cc.
		Difference, 0.05 cc.	

These results are about as good as could be desired.

Experiment No. 8. Determination of soda combined as soap in a commercial sample whose approximate composition was known. Soap taken, 5.7373 gms. Dissolved in large volume of neutral alcohol and added some phenol-phethaleïn as indicator. There was no alkaline reaction on boiling (this is necessary to decompose any bicarbonate which would give us indication with phenol-phthaleïn) and so caustic and carbonate or bicarbonate must be absent. Added blue lacmoid solution and proceeded with the titration in the boiling hot solution. (The indication appears better in a hot solution.)

	Burette reading.	Corrected reading.
HCl used	12.14 cc.	12.07 cc.
Equivalent to 0.37834 gms. of soda = 6.59% of the soap.		

To check this result 5.494 gms. of the soap were ignited in a platinum dish and the residue of sodium carbonate titrated.

	Burette reading.	Corrected reading.
H_2SO_4	11.63 cc.	11.60 cc.
Equivalent to 0.36311 gms. of soda = 6.61% of the soap.		
Result by direct titration		6.59% of soda.
" " ignition and titration		6.61% " "
Difference, 0.02%—a close check.		

In conclusion, I would say that while this process may not be used in all cases, it will be found of great convenience in many.

* Being the excess used.

† Due to the sodium carbonate.

CONCERNING THE CONSTANT TO BE USED IN CLERGET'S INVERSION PROCESS

To the Editor of The Journal of Analytical and Applied Chemistry

In the May number of your excellent journal Mr. Theodore Breyer, of the firm of Breyer and Schweitzer, New York, in animadverting upon the action of the Association of Official Agricultural Chemists at its last meeting with regard to the constant to be employed in connection with Clerget's method of inversion, also took occasion to criticise a report on methods of sugar analysis issued by the Louisiana Sugar Chemists' Association nearly three years since.

Being one of those whom Mr. Breyer has seen fit to designate "sugar polarizators," and having been chairman of the committee which prepared this report, I ask space in your journal to reply to some of his criticisms.

His letter to *The Sugar Cane* of March 1898 had not been previously brought to my notice, nor was I aware that the report referred to had appeared in the January number of the same journal, though it was reprinted in a number of other periodicals about that time.

The *Report on Methods of Sugar Analysis of the Louisiana Sugar Chemists' Association* was prepared by a committee of that Association for the direction and guidance of chemists engaged in the chemical control of sugar houses in Louisiana, and the work of the committee was confined chiefly to the investigation of methods then generally in use among the sugar chemists of this state.

In the first few lines of that report it was stated that the work was undertaken "with a view to the improvement of the present methods of sugar analysis and the elimination of errors in the processes now employed in the determination of the constituents of cane juices, syrups, molasses, etc."

The methods referred to as being employed at that time in the analysis of sugar products were chiefly those in Tatter's *Manual of Sugar Analysis*, and the inversion process as therein given was the one generally followed by chemists where [illegible]

polarization was resorted to. Although this was termed Clerget's process, it differed, like many other modifications of the method, (which, nevertheless, bear Clerget's name), somewhat in details from the method as originally carried out by Clerget himself.

This process is included in the methods of analysis given in the pamphlet referred to, and provided that the sample, after addition of the acid, should be heated in a water bath at 68°–75° C. for a period of fifteen minutes. It will be observed that a range of several degrees of temperature above 68° C. is permitted, while the time of heating is somewhat longer than is prescribed in Clerget's method as originally executed. In connection with this method as described in the pamphlet above alluded to, it was recommended that "in calculating the true per cent. of sucrose from the data *thus* obtained [*i. e.*, by the use of the method just described] instead of Clerget's original constant of 144, the revised figure of 142.4 should be used."

The object of the experiments of the committee as stated at a meeting of the Association and as reported in the *Louisiana Planter*, was not to attempt to prove or disprove the correctness of the number 144 as used in connection with Clerget's original method, but to determine what figure should be used in conjunction with the method then generally employed.

It is a fact well known to those who have had occasion to make numerous experimental inversion tests, that the rotary power of invert sugar solutions is much affected by the degree of heat employed in inversion and the length of time for which the heat is continued, and at a given temperature the invert reading is found to decrease in quite a marked ratio the longer the heat is maintained after inversion is effected. A large number of tests which I have made show even higher readings than those obtained by Clerget, when the solution has been kept at 68° C. for from two to four minutes only, but the longer the heat was continued, the lower became the reading.

While Gubbe and others, as Mr. Breyer states, have shown that the degree of concentration of an invert sugar solution influences quite appreciably its rotary power, A. Wohl (*Ber. d. chem. Ges.*, **23**, 2084) shows that with a relatively larger proportion of acid employed in inversion, the left handed reading of

the solution is decreased instead of being increased and the greater the length of time the heat is maintained the lower the comes the reading. So the value of the constant to be used in calculating the results of inversion tests is largely determined by the temperature employed and length of time of digestion of the solution

The results reported in the pamphlet referred to were secured by myself, with the co operation of two chemists who had had considerable experience in sugar analysis as well as in other branches of chemical work, and I have since made many tests which corroborate these results, the process in each case being carried out in the manner described above

In recommending the change from 144 to 142.4 the reporter Dr. Stubbs, did not intend, so I understand that the time of heating in inversion should remain at ten minutes as in the original Clerget method, but that the time employed should be twenty minutes as in the method published in the proceedings of 1888, and as in the elective methods given in the proceedings of 1890 the omission of the correction as to time of heating being through inadvertence

Dr Stubbs report to the Association in 1888 on the subject of sugar analysis with the references therein given and the large amount of work done under his direction in the laboratories of the experiment stations of this state in the investigation of this very subject constitute a sufficient refutation of the charge of lack of knowledge of the chemical literature and of the facts bearing upon this question

As to the low reading of the normal sucrose solution at 20° I will say that I had at hand the very references to which Mr Brewer speaks at the time this work was being done and was fully aware of the results of the experiments of other chemists The results were stated as noted accurately by three chemists of experience in polariscope work and were merely corroborative incidentally along with other statements made and not with the intention of advancing a new theory or opinion with regard to the polarization of sucrose solutions at low temperatures

In conclusion I would say that although Mr Brewer states that it is surprising that after this publication has been

The Sugar Cane] such a method should be proposed and accepted as a standard," nevertheless we find that Sidersky in his voluminous work (Traité d' Analyse des Matières Sucrées, Paris, 1890) incorporated in full the table for the calculation of double polarization results as published in the report of the committee above referred to. We find also that Spencer in his *Hand Book* recommends the use of the constant of Wohl (142.7). Babington (*Analyst*, October, 1891) speaks of employing the same number, while Weichmann endorses the constant of Hertzfeldt (142.66); so that the substitution of a new constant for the 144 of Clerget is not a new departure, especially where somewhat different conditions obtain. At any rate it is at least certain that "all the chemists in the sugar industry" do not use Clerget's original formula, as Mr. Breyer would have the readers of your journal infer.

Very respectfully,

B. B. Ross.

CHEMICAL LABORATORY, STATE UNIVERSITY,
BATON ROUGE, LA., JULY 18, 1892.

POTASSIUM TETROXALATE AS A STANDARD IN ACIDIMETRY AND ALKALIMETRY.*

BY BERTRAND C. HINMAN.

Tetroxalate of potassium, (KHC_2O_4, $H_2C_2O_4$, $2H_2O$), was originally proposed for this purpose by Ulbricht and Meissl, *Pharm. Centrh.* [N. F.], **6**, 198, and commended by Kissling, in the *Zts. f. angew. Chem.*, 1889, 332.

At the 1890 meeting of the Association of Official Agricultural Chemists (*Eighth Annual Report*, p. 24) it was adopted as the alternate substance for standardizing. At the meeting of 1891 (*Ninth Annual Report*, pp. 131 and 153) it was the subject of considerable argument but was retained as the alternate for another year.

An investigation has been made of the properties of the salt with a view of determining its availability for this purpose.

The requisites for a substance to be used for standardizing are that it should be easily obtained pure, of definite chemical

* School of Mines Quarterly, July, 1892.

composition, that it should remain unaltered in the air and react sharply with indicators.

Potassium tetroxalate is soluble in forty parts of cold and in six parts of boiling water (Storer, *Dic. Sol.* p. 428).

Ignition converts it to K_2CO_3, so it would seem to be valuable for standardizing both acid and alkaline solutions.

The formula given requires

$$(H_2O = 14.173 \text{ per cent})$$
$$\text{Equivalent to } H_2C_2O_4 = 70.866 \text{ per cent}$$
$$\text{Equivalent to } K_2CO_3 = 27.165 \text{ per cent}$$

It may be prepared by uniting solutions containing proper proportions of $K_2C_2O_4.2H_2O$, and $H_2C_2O_4.2H_2O$, crystallizing out and purifying by recrystallization. Three repetitions are said to be amply sufficient to produce a pure substance.

This method was followed, and an examination made of three lots of the salt, that crystallized four times, a mixture of that crystallized twice and thrice, and the crystals obtained from a concentration of the mother liquor.

Determinations of the oxalic acid in these samples were made by precipitation as CaC_2O_4, weighing as $CaSO_4$, and by titration with KOH standardized by the usual method.

The results were as follows:

[illegible]	Method	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]		[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]
	KOH	[illegible]		[illegible]	[illegible]
		[illegible]		[illegible]	
		[illegible]		[illegible]	
[illegible]		[illegible]		[illegible]	[illegible]
				[illegible]	
[illegible]				[illegible]	[illegible]

The salt was also tested by standard permanganate and gave results too high. All the samples analyzed were found to contain over one per cent. [illegible] the more the number of recrystallizations, the greater is the excess found.

The mixed samples crystallized twice and thrice was again recrystallized three times and tested with the standard KOH

The percentage of oxalic acid was 73.32; apparently no change in composition had taken place.

An effort was made to determine the water of crystallization by heating the substance in an air-bath at given temperatures for specific times.

The following results were obtained:

SAMPLE.	Time of heating, in hours.	Temp. ° C.	Weight taken.	LOSS.	Per cent. of loss.
Cryst. 4 times.....	3½	80	1.0433	0.1483	14.214
" "	3½	100	1.0433	0.1504	14.416
" "	3½	128	1.0433	0.1656	15.783
" "	6	128	1.0090	0.1691	16.758
" "	9	128	1.0090	0.1740	17.240
" "	11	128	1.0090	0.1789	17.730
" "	3	95	0.7527	0.0980	13.020
Cryst. 2 and 3 times.....	3½	80	1.2680	0.1768	13.936
Cryst. 4 times.....	3	100	0.7527	0.1103	14.680
Cryst. 2 and 3 times.....	3½	100	1.2680	0.1823	14.377
" " "	3½	128 160	1.2680	0.2348	18.510
" " "	6	128	1.0682	0.1683	15.755
" " "	9	128	1.0682	0.1749	16.374
" " "	11	128	1.0682	0.1789	16.728

These figures do not show a satisfactory result, and indicate that the combined water cannot be determined by heating.

Evidently a temperature of over 100 C. causes a decomposition, for in every instance at that temperature the salt lost more than its theoretical percentage of water of crystallization, and at somewhat higher temperatures the loss was considerable, and at a constant temperature increased with the time.

This phenomenon was easily perceptible at 128° C., at which temperature Bornträger (*Fres. Zts.*, **31**, 43) says the salt must be heated to insure perfect drying.

Yet in these experiments it was found that eleven hours' heating at this temperature caused a loss of over 3.5 per cent. more than the theory for water. It is thus evident that the salt cannot be heated to this temperature without suffering decomposition.

In order to determine whether the apparent excess of water might be due to hygroscopic moisture, and whether or not the salt was efflorescent, a weighed portion in a tared dish was moistened with a few drops of distilled water and set aside in a desiccator over concentrated sulfuric acid. After this treatment,

if the dish with its contents should weigh less than it did before wetting, it would indicate either that the salt was non-efflorescent, and contained hygroscopic moisture, or that it was dry, but would effloresce in dry air. But the dish rapidly regained its original weight, and remained persistently at that point for three days, at the end of which time the observations were discontinued. Apparently, then, the salt was dry and was non-efflorescent.

From the results of the determinations of the equivalent oxalic acid, it would be expected if the water was out of proportion that it would be low, but experiment has shown that the equivalent oxalic acid and water are both high.

As a matter of fact, not much faith is to be placed in the water determinations, for the experiments reasonably justify the belief that the estimation of the water of crystallization cannot be accurately made by determining the loss on heating.

The ignition of several samples of the salt, weighing and titrating the resulting K_2CO_3 with sulfuric acid (standardized by sodium carbonate), using methyl orange as an indicator, gave the following results:

SAMPLE.	Weight taken.	K_2CO_3 by weight.	K_2CO_3 per cent.	K_2CO_3 by titration.	K_2CO_3 per cent.
Cryst. 4 times.....	1.0433	0.2817	27.000	0.2774	26.588
" "	1.0090	0.2717	26.927	0.2732	27.076
Cryst. 2 and 3 times.....	1.2680	0.3430	27.050	0.3409	26.884
" " "	1.0682	0.2890	27.083	0.2863	26.803

The average of the percentages obtained by weighing is 27.015, and by titration, 26.838.

These figures coinciding quite closely with the theoretical, and the acid being high, indicates a curious balancing between acid and water. For if the K_2O be correct and the acid high, then the water must be low. But as the water determinations could not be satisfactorily made by the method tried, this conclusion is unverified.

These results being so far at variance with theory, another sample of the substance was very carefully prepared in the same manner as the first and tested as before. As usual, the purified salt after being filtered from the mother liquor was pressed

between filter paper to remove the superfluous moisture, and then spread out on fresh paper in a layer not over a quarter of an inch thick and left to dry for three days.

In order to determine whether all the hygroscopic moisture had been removed by this treatment, a weighed portion of the material thus dried was placed in a tared dish, and allowed to remain in a desiccator over sulfuric acid for three days. The loss was 0.728 per cent. At the end of six days it was 1.23 per cent., and a week later, or after having been in the desiccator for about two weeks, the loss amounted to 3.58 per cent. At the end of eight weeks there was a loss of 11.41 per cent. The crystals had by this time assumed an opaque appearance, and efflorescence was clearly taking place.

Therefore it is clear that by this procedure a determination of the hygroscopic moisture is impossible, for the salt effloresces, and, moreover, the experiment seems to show a contradiction to the observation deduced from a previous experiment made under conditions almost similar, when the tetroxalate refused to part with any of its water of crystallization in a desiccator over sulfuric acid. The only difference between the two experiments was that the samples of salt operated upon were produced at different times, though the effort was in the second preparation to duplicate the method employed in the first.

This second preparation lost, upon heating for three hours at 100° C., 14.370 per cent., but upon standing under a bell glass for several days it gained 1.466 per cent. of water from the air. Thus when the salt is nearly anhydrous it is deliquescent, and when containing its full amount of water of crystallization its tendency is to effloresce.

An average of three titrations of this second preparation with $\frac{n}{10}$ KOH gave an equivalent of 73.88 per cent. of oxalic acid, which is two per cent more than was found in the first sample, and three per cent. more than theory calls for. Upon ignition, there was left a residue of K_2CO_3 amounting to 27.131 per cent., which is almost precisely the theoretical. Careful tests for bases other than potassa gave negative results.

In the use of indicators for determining the end reaction in these titrations, there seems to be some doubt as to which of the

many in use is the best. The Association of Official Agricultural Chemists recommends methyl orange, although it is generally accepted that it does not react sharply with organic acids and upon trial the results were very uncertain. Phenol phthalein works perfectly, and is certainly the best indicator for this purpose which is available, although litmus properly prepared is said to give good results. Coralline, or rosolic acid, cochineal, carminic acid, and congo red, are of no value at all as indicators with oxalic acid.

As a result of these experiments it is clear that tetroxalate of potassium, as prepared by the directions of those who advocate its use, is not a substance of constant composition. The variations from the theoretical figures are so great as to entirely exclude its use as an agent for standardizing solutions for volumetric analysis. This conclusion is justified by the preceding experiments, and finds verification by many who have investigated the subject.

In this connection may be quoted the remarks of Mr. William Frear on page 131 of the *Proceedings of the Eighth Annual Convention of the Association of Official Agricultural Chemists*, where he says: "The method by tetroxalate of potash was not employed because it was found impossible to get a perfectly constant salt, and because in our experience even with dimethyl amidoazobenzene orange as an indicator, it was not possible to get a perfectly sharp end reaction. A tetroxalate prepared under my direction last year by Dr. McDonnell by dissolving together the proper proportions of chemically pure acid potassium oxalate and oxalic acid gave, after the fourth crystallization, results showing it to possess an acidity 1.17 per cent greater than that sent to Dr. Caldwell for comparison of standards, and which, according to the latter and Mr. Scovell, stated to agree exactly in strength with their acids standardized with $AgNO_3$. Another sample obtained from Baker and Adamson, when precipitated as CaC_2O_4 and weighed as CaO, gave only 7.55 per cent of the calculated amount of the latter oxide as in a mean of three closely concordant determinations."

Further confirmation is found in the experiments of Mr. H. W. Wells (JOURNAL OF ANALYTICAL AND APPLIED CHEMISTRY,

6, 192), who says, "Tetroxalate of potassium possesses all the disadvantages that pertain to all the above mentioned reagents. It is harder to purify than soda, and it weathers as readily as oxalic acid."

It is evident then that the salt is indefinite in character, uncertain in quality, and cannot be prepared, by the methods given, of such purity as to be of service for the purpose for which it is recommended.

THE ASSAY OF TIN.*

By Edmund H. Miller, Ph.B., A. M.

The work described in this article was undertaken for the purpose of ascertaining the best methods of assaying tin ores and also to compare the results obtained by the numerous different methods on the same ore. In order to have a check on the assays it was necessary to have an accurate analysis of the ore; to be certain of which, the various methods of analysis were tried and then duplicates were run on the one which seemed best, and the average of these results was taken as representing the true amount of tin in the ore. This figure was 65.62 per cent.

The assay of tin ore is in reality the assay of cassiterite, for the other minerals containing tin are too rare to be of economic importance.

The ore was stream tin from Durango, Mexico, contained some topaz and 8.26 per cent. of oxid of iron. The ore was ground to 80-mesh, then very thoroughly mixed and sampled for analysis.

I. The Analyses.

The first method of analysis tried was the reduction by hydrogen in a Rose crucible.† One gram of finely ground stream tin was placed in a small porcelain crucible and heated red-hot for four hours while a current of hydrogen was introduced through the top of the crucible. The residue was treated with concentrated hydrochloric acid, tranferred to a beaker, boiled, then diluted and filtered.—Residue A.

* School of Mines Quarterly, July, 1892.
† *Crookes' Select Methods*, p. 406.

The filtrate was neutralized with ammonia and the precipitate dissolved in a little sulfuric acid, so that the solution was slightly acid, then the tin was precipitated by hydrogen sulfid as dark brown SnS, —the precipitation was done in the cold and was found to be complete: the precipitate was filtered and washed with a dilute solution of ammonium chlorid ignited and weighed as SnO_2, after treatment with nitric acid

Residue A was dried, burned and heated as before in a current of hydrogen for one hour, then treated with concentrated hydrochloric acid, diluted, filtered, etc., and saturated with hydrogen sulfid,—the precipitate which formed was kept separate from the first and was washed, dried, roasted, and weighed

As the amount of tin obtained by the second reduction was very considerable, a third treatment was made on the residue from the second reduction. As a result, a little more tin was obtained. A fourth treatment showed that all the tin had been removed that was possible under these conditions Results were as follows

Residue A weight	[illegible]
B	[illegible]
[illegible]	[illegible]
Total percentage SnO_2 [illegible]	
Equivalent [illegible] per cent tin	

These results were so unsatisfactory that the method was not investigated further

Reduction by means of granulated zinc* and hydrochloric acid was also tried, but without success owing possibly to the presence of a piece of platinum foil which is claimed to greatly assist in the efficiency of the reduction

The next method was that recommended by Rose.*

One gram of the ore was mixed with three grams of sulfur and three grams of carbonate of soda and fused for one hour and a half in a porcelain crucible the mass was then treated with water which almost all dissolved to a very dark green solution the residue consisted of iron sulfid silica and undecomposed stream tin The solution was filtered and the filtrate filtered

* [illegible]
* [illegible]

and acidified with sulfuric acid, which produced a copious yellow precipitate of stannic sulfid, SnS_2; this was filtered, washed with hot water, dried, roasted with ammonium carbonate and then treated with nitric acid and weighed as SnO_2.

The residue was treated with hydrochloric acid to remove the iron sulfid, then burned, mixed with carbonate of soda and sulfur and re-treated; the mass was treated with water as before, and precipitate of SnS_2 was obtained; a third fusion gave no more tin. Results were as follows:

	SnO_2.
First fusion weight	0.7958
Second fusion weight	0.0360
Total fusion weight	0.8318
Equivalent to tin	0.6569

This method was next tried, using with one gram of the ore five grams of sulfur and five of soda; the object was to see if by increasing the amount of flux the second fusion could be avoided. The tin sulfid was also redissolved in ammonium sulfid as it was found some iron sulfid was dissolved by the sodium sulfid solution.

This method gave 0.7676 gm. of tin oxid.

The above method (redissolving the SnS_2), was then tried, but with Rose's proportions of flux, having first ground the ore as fine as possible in an agate mortar. The result was 0.7662 gm. of tin oxid, which seemed to check the previous method very well, but to make sure that all the tin was out of the residue, it was treated again and 0.0716 gm. more SnO_2 obtained, giving a total of 0.8378. This result is nearly that obtained by the first trial and goes to show that all the tin in cassiterite cannot be decomposed by one fusion.

The third method tried was fusion with acid potassium fluorid; one gram of the ore was mixed with five grams of acid potassium fluorid and fused at a bright red heat in a platinum crucible for twenty minutes; the mass melted very readily, and the fusion was as clear as water. After cooling it was removed from the crucible and boiled with hydrochloric acid; the acid did not attack the cake easily, and some time was spent in getting it into solution; it was then filtered. Attempts were made to precipitate the tin as oxid in this filtrate by boiling with sulfuric

and with nitric acid, but were unsuccessful; the filtrate was then made acid with acetic acid and the tin precipitated by hydrogen sulfid; the precipitate was black and contained iron; this was filtered, treated with strong ammonium sulfid and the sulfid of tin precipitated from the double sulfid solution by neutralizing with sulfuric acid; the yellow stannic sulfid so obtained was filtered, washed, dried, roasted, treated with nitric acid and weighed as oxid of tin: weight, 0.7070 grams.

This method was tried again, the fusion being kept up for one hour; the mass was partially dissolved by water which attacked it more quickly than hydrochloric acid, then boiled with hydrochloric acid to dissolve the iron. After filtering the solution was made alkaline with ammonia, and then acid with sulfuric and saturated with hydrogen sulfid; the precipitate was treated as before; weight of SnO_2, 0.7688 grams.

This method was a third time tried and the residue re treated; this showed that all the cassiterite was not decomposed by one fusion.

The results by this method did not compare at all favorably with those from the fusion with carbonate of soda and sulfur; besides it required repeated fusions to decompose the ore, involving a loss of tin on account of the volatility of the fluorid.

A modification of Rose's method* was next tried using carbonate of potash instead of carbonate of soda; one gram of the ore was mixed with 3 grams of K_2CO_3 and 3 grams of sulfur and fused for forty-five minutes in a porcelain crucible; the mass was dissolved in water and gave a yellow solution free from iron sulfid instead of the dark green solution from the soda and sulfur fusion; the rest of the operation was conducted as before, the residues being ground fine in an agate mortar each time they were re treated. Results were as follows:

[illegible]

* [illegible]

I consider this method upon the whole the most accurate and satisfactory, although it is not a rapid one.

COMPARISON OF RESULTS.

		SnO_2.	Sn.
1	Rose crucible hydrogen,	68.55	53.88
2	Na_2CO_3 and S residue re-treated,	83.18	65.43
3	Na_2CO_3 and S residue not re-treated,	76.76	60.32
4	Na_2CO_3 and S residue not re-treated,	76.62	60.27
5	Na_2CO_3 and S residue re-treated,	83.78	65.90
6	KHF_2,	79.70	62.69
7	KHF_2,	76.88	60.37
8	K_2CO_3 and S residue re-treated,	83.30	65.53
	Average of 2, 5, and 8,	83.42	65.62

II. *a.*—ASSAY METHODS GIVING TIN BUTTONS.

*German Method.**—Five grams of the ore was mixed with one gram of very finely ground charcoal and placed in the bottom of an ordinary Hessian crucible, No. 5. Over this was placed fifteen grams of black flux substitute mixed with one gram of borax (the black flux substitute is made by mixing ten parts $NaHCO_3$ with three parts flour), then a cover of salt, and on this several lumps of charcoal. The crucibles were put in a coke crucible fire and left there one hour and twenty minutes at a good heat. The slag was clear, well fused and dark brown; the buttons weighed 3.10 and 3.29 grams, respectively (Nos. 1 and 2).

Doubling the above charge was then tried, but in all other respects the assay was run in the same way. Buttons weighed 6.465 and 6.250 (Nos. 3 and 4).

The next assays were made in the same way but a lower heat was used, giving a lower result. Slag was brown, well fused. Time, one hour. Weights of buttons, 5.060 and 5.370 (Nos. 5 and 6).

No. 7. Same charge but hotter fire; gave good button weighing 6.365. Nos. 8 and 9. These assays were made in a charcoal-lined crucible. Ten grams of ore and two grams of charcoal were mixed together and put in the bottom, then covered with a mixture of twenty grams of black flux substitute and one of borax glass, then lumps of charcoal. The assays were heated as usual; they were unsuccessful, as the porous lining seemed to absorb all the slag, so that the button did not collect well.

* Last cit. Glass, *Metallurgische Probirkundst*, Leipsic, 1882, p. 412. Kerl-Batty, *Die Probirkunde*, Brunswick, 1879, p. 391.

Nos. 10 and 11 were an experiment, as five grams of argol were substituted for the flour in the black flux substitute. The charge was as follows: Ore, 10; charcoal, 2; argol, 5; soda, 2; borax glass, 1. Salt cover, charcoal. They were fused in a hot fire for three-quarters of an hour. Weight of buttons [illegible] and 3.25 grams.

Nos. 12 and 13 were run in charcoal-lined crucibles with the following charges: Ore, 5 grams; B. F. S., 15 grams; borax glass, 1 gram; charcoal, 1 gram; salt cover, lump charcoal. Time, one hour; good reduction, but buttons failed to collect well. Results practically same as Nos. 8 and 9.

Nos. 14 and 15. Charge same as 3 and 4 but fire very hot (white heat). Time, one hour. Buttons, 6.422 and 6.[illegible]; This shows that it is possible to reduce iron by the German method if the charges are heated to a white heat.

Nos. 16 and 17. Same as 15 and 16 but moderate fire. Buttons, 6.281 and 6.278.

I then tried the German method in the muffle furnace using flat bottomed crucibles. Charge same as 1 and 2. Time, [illegible] five minutes. White heat. Weight of buttons [illegible] and [illegible] (Nos. 18 and 19).

COMPARISON OF RESULTS

No.	Minutes	Fire	Slag	Percentage
	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]			[illegible]
	[illegible]			[illegible]
[illegible]	[illegible]			[illegible]
[illegible]	[illegible]			[illegible]
[illegible]	[illegible]	White heat		[illegible]
[illegible]	[illegible]			[illegible]
	[illegible]	Medium		[illegible]
	[illegible]			[illegible]
Average				[illegible]

I believe this to be one of the best methods of determining tin in a high grade ore. To be run successfully a long time, one hour, and a hot fire between a bright red and a white heat but not as hot as a white heat are necessary. I think good results may be obtained in the muffle by this method.

[illegible] The first three assays by this method were made with a very poor quality of wood such as is used for [illegible]

amalgamation. Charge was: Ore, 10 grams; 5 grams cyanid put in bottom of crucible; 25 grams cyanid mixed with ore and placed on top, then a cover of 5 grams of cyanid and a cover of salt. The charges were heated up slowly and left in a moderate fire for twenty minutes after fusion. Weights of buttons were as follows: No. 20, 5.78; No. 21, 5.840; No. 22, 5.675.

Five assays were next made using different amounts of cyanid and mixing it all with the ore. The object was to ascertain what quantity of cyanid it was necessary to use and also to see whether the layer of cyanid in the bottom and on top was advantageous.

In each case ten grams of the ore was used and the charge heated in a good fire for twenty-five minutes.

No.	Grams Cyanide.	Weight Button.	Percentage.
23	10	1.744	17.44
24	20	4.170	41.70
25	30	4.941	49.41
26	40	5.073	50.73
27	50	5.195	51.95

These assays show that up to fifty grams the amount reduced increases with the amount of cyanid used, and also that the layers of cyanid top and bottom are necessary. Nos. 28 and 29. Ore 10 grams; 5 grams KCN in grams, then 30 grams mixed with ore, then 5 grams KCN, then salt cover—ordinary unlined Hessian crucibles were used—as in previous assays. Charges were heated for one hour in a hot fire. The cyanid used was of a better quality than that employed in the first assays. Slag was dark green and well fused. Weights of buttons were 6.295 and 6.860. Nos. 30 and 31 were run as above, except that chalk-lined crucibles were used. The slags were light green, porous, and pasty. Buttons weighed 5.300 and 6.030.

Nos. 32 and 33 were run with some charge in a hot fire for forty-five minutes. Slag was green. Buttons weighed 6.683 and 6.442.

Nos. 34 and 35 same as above, except in chalk-lined crucibles. No. 34, slag porous. Result low. No. 35, slag green. Button weighed 6.842.

No. 36 was run in an unlined crucible with the usual charge, but with chemically pure cyanid (98 per cent. KCN) in as hot a fire as possible. Slag was white. Button weighed 7.089.

No. 37 same as No. 36, but in chalk lined crucible [illegible] both, 45 minutes. Weight button, 7.192.

Nos. 38 and 39 same charge, but low heat. No. 38 [illegible] crucible. Weight button, 6.870. No. 39 chalk lined [illegible] 6.315.

Nos. 40, 41 and 42 same charge, except no salt cover [illegible] cyanid being used. Moderate fire, time thirty minutes [illegible] gray. Weights, No. 40, 6.193; No. 41, 6.018; No. 42 [illegible] Buttons were well formed, bright and fairly soft.

Nos. 43, 44 and 45 same as previous, but pure [illegible] No. 43, 6.938; No. 44, 6.896; No. 45, 6.812. Buttons were [illegible] The next assays were run to test the merits of the salt [illegible] the usual charge was used (ordinary cyanid). Nos. 46 [illegible] had salt covers. Nos. 48 and 49 had not. Nos. 46 and 48 [illegible] in one fire and 47 and 49 in another, so the conditions were [illegible] same in the case of those with and without salt covers. We [illegible] No. 46, 6.362; No. 47, 6.509; No. 48, 6.970; No. 49 [illegible]

This seems to me to be sufficient to show the advisability [illegible] using a cover of salt.

I next tried some assays to see if a mixture of [illegible] substitute and cyanid would give satisfactory results [illegible] that it would not.

No. 50. Ore, 10 grams; KCN, 5 grams; [illegible] 20 grams, and B. F. S., 10 grams, mixed with ore; then KCN, 5 grams, salt cover. Moderate fire, thirty minutes. Slag [illegible] Button weighed 6.005. No. 51 same as No. 50 except KCN [illegible] grams; B. F. S., 15 grams, mixed with ore. Weight [illegible] 6.045. No. 52 same as No. 50 except KCN [illegible] grams; [illegible] 20 grams, with ore. Weight of button, 5.788. No. 53 same as No. 50, but time forty-five minutes on a rather hot fire. Weight of button, 6.160. No. 54 same as No. 53 except KCN [illegible] grams; B. F. S., 20 grams. Weight of button, 5.7[illegible]. No. 55 same as No. 53 except B. F. S., 30 grams. Weight of button [illegible]

From the assays by the cyanid method it seems that [illegible] chalk lined crucibles are objectionable because they [illegible] fusion pasty at a low temperature, giving a pasty slag [illegible] if the heat is raised so as to fuse them iron is reduced [illegible] renders the results too high. Second, chemically pure cyanid [illegible]

reduce iron at a lower temperature than the ordinary cyanid; third, a salt cover is necessary; fourth, the layer of cyanid on the bottom and top of the charge is a decided advantage.

I also tried running cyanids in the muffle, the following charge being used. Ore, 5 grams, KCN, 5 grams on the bottom, then 25 grams mixed with the ore, then cover of cyanid, then salt and finally lumps of charcoal. They were kept in a hot fire for twenty minutes; the buttons were good.

No.	Weight button.	Per cent.
56	3.218	64.36
57	3.443	68.86

Cryolite Method.—Was tried as follows: Ore, 10 grams, cryolite, 10 grams, charcoal, 2 grams, mixed together and put in naked crucible, and covered with salt and charcoal; heated in crucible fire; result, no buttons and no apparent reduction (Nos. 58 and 59).

II. *b.*— ASSAY METHODS GIVING ALLOYS FROM WHOSE WEIGHT THE AMOUNT OF TIN CAN BE CALCULATED.

Bronze Buttons. * —First method. Oxid of copper and black flux substitute. Nos. 60 and 61. Ore, 10 grams, oxid of copper (CuO), 10 grams, black flux substitute, 40 grams, borax glass, 1 gram, were mixed together and put in an unlined Hessian crucible, and then a cover of salt added; the crucible was placed in a hot fire and the charge fused for one hour; the slag was dull green and well fused, buttons weighed 13.13 and 12.82 grams; subtracting the amount of copper in 10 grams of oxid of copper, 7.97, gives the weight of tin 5.260 and 4.850. Nos. 62 and 63, same as above except crucibles were lined with chalk; weight of tin in buttons, 5.600 and 5.250. Nos. 64 and 65. Ore, 10 grams, B.F.S., 10 grams mixed and put in a charcoal-lined crucible, covered with lumps of charcoal; crucibles were heated as before one hour in a hot fire; there was very little slag as most was absorbed by the lining. Weights of buttons, 14.02 and 13.85, equivalent to 60.50 and 58.80 per cent. of tin.

These results corroborate those obtained by cyanid and black flux substitute, and show that black flux substitute is not a proper reducing agent for cassiterite under any conditions.

* Hofman, p. 37. Winkler, *Berg und Huttenmännische Zeitung*, 1864, p. 17. Mitchel, p. 411.

Oxid of Copper and Cyanid of Potassium.—Nos. [illegible] and [illegible]. Five grams of cyanid were placed in the bottom of an ordinary No. 5 Hessian crucible, then 30 grams of cyanid was mixed with 10 grams of the ore and placed on top; then a cover of cyanid (no salt). Charge was heated for one hour in a fairly hot fire; the slag was stony and gray; buttons were bright and well shaped. No. 66 weighed 13.7060; No. 67, 13.4800; equivalent to 5.796 and 5.490 (subtracting 7.97). Nos. 68 and [illegible] same as above but run in chalk lined crucibles; slag was porous and buttons were not well shaped; weighed 13.72 and [illegible] 5.750 and 5.920.

Two assays were run in unlined crucibles with same [illegible] and salt cover, and with them a blank assay to determine the real amount of copper reduced (Nos. 70, 71, and 72).

No.	Weight [illegible]
[illegible]	[illegible]
[illegible]	[illegible]

The weight of copper button from the blank assay [illegible] this is very much below the theoretical amount of copper [illegible] 7.97, and accounts for the low results in assays Nos. [illegible] and [illegible]; subtracting the weight of copper obtained from the blank [illegible] the weight of these bronze buttons I get as follows: No. [illegible] 6.370; No. 67, [illegible]; No. 68, 6.330; No. [illegible].

In this method the disadvantage of the chalk [illegible] the weight of the buttons, but in the porous and [illegible] of the slag and in the irregular form of the buttons.

Had a blank assay been run with the black flux [illegible] assays better results would have undoubtedly been obtained; but the weights were so low that the method did not seem [illegible] further investigation.

II. ASSAY METHODS GIVING AN ALLOY [illegible] BY WET METHODS.

Copper Oxid and Cyanid.—Two grams of the ore [illegible] with ten grams of cyanid and placed in a small Hessian [illegible] on a layer of cyanid, and then covered with a second [illegible] as usual; then salt cover, and heated in a hot fire three quarters of an hour.

Three assays were run in this way; the results [illegible]

(Nos. 72, 73, and 74). The buttons were then treated with nitric acid and the oxid of tin weighed; the percentage of SnO_2 was 81.26, equivalent to 63.92 of tin.

	Grams.
Average weight of bronze buttons	4.857
Average weight of tin subtracting theoretical amount of Cu in 5 grams CuO	0.872
Average weight of tin subtracting Cu as found in blank assay	1.159
Average weight of tin in buttons as calculated from weight of SnO_2	1.2784

This method of using copper as a collecting agent for the tin is recommended for low grade ores as it prevents the loss of small particles of tin in the slag.

From the foregoing experiments there seem to be four methods of assaying cassiterite which give sufficiently accurate results for practical work—the German method, cyanid, oxid of copper and cyanid when blank assay is run, oxid of copper and cyanid when button is treated with nitric acid and the oxid of tin weighed.

Assays of tin should always be run in duplicate and the average, not the highest, taken.

In the German method an hour in a fire almost at a white heat gives the best results.

Cyanid Method.—The following charge is the best. KCN 5 grams in bottom of crucible, then 30 grams mixed with the ore, then cover of 5 grams more, then salt cover; used on unlined crucible and heated at a red heat (not a bright red) for twenty to twenty-five minutes. The results obtained using this charge were as follows:

No.		Per cent.
32	Ordinary KCN, hot fire, 45 minutes, salt cover.	66.83
33		64.42
46	Ordinary KCN, low heat, 30 minutes, salt cover.	63.62
47		65.90
Average		65.19

Oxid of Copper and Cyanid.—Use same charge as in cyanid method, adding 10 grams of black oxid of copper; heat in a hot fire for three quarters of an hour; with every set of assays run one with same charge, leaving out the ore, and subtract the

weight of the copper button from the weights of the bronze [illegible]
Results by this method:

No.	[illegible]	[illegible]
"	[illegible]	[illegible]
"	[illegible]	[illegible]
Average		[illegible]

In the method where the bronze button is dissolved in [illegible] acid it is not advisable to get too large a button on account of the time taken in dissolving it. I would recommend taking such amounts of ore and oxid of copper as to give a button of about three grams, of which over two grams should be copper.

There are several other methods of assaying tin [illegible] and many more to be found by consulting the literature on the subject, but they all seemed less feasible than the ones described.

One very important point in connection with the assay [illegible] ores is the concentration of a large sample down to [illegible] containing the tin for assay; this may be done in a [illegible] coarse jigging. The high specific gravity of [illegible] this comparatively easy.

NOTES ON SILICON IN FOUNDRY PIG IRON.

During the [illegible] while acting as chemist at the furnaces operated by Andrews and Hitchcock at Hub[illegible] it was my duty to make daily determinations of the [illegible] each cast of pig iron made from two furnaces. While [illegible] tion was thus primarily directed to the chemical composition [illegible] the iron, it was my habit to observe also the corresponding [illegible] tions in its physical appearance. It is of these [illegible] chemical composition and of their correlation with the [illegible] of the iron and with other physical peculiarities that I [illegible] to treat. [illegible]

opinions herein expressed, save where an accepted theory is quoted, are to be taken simply as *obiter dicta*.

The pig iron manufactured at the Hubbard furnaces has held for more than twenty years an enviable reputation as a foundry iron. Its composition is such that it seems to combine in an unusual degree the different requirements of softness, fluidity, and strength. It is largely purchased by eastern manufacturers of light castings, such as stove fixtures; and in many cases where a softener is required is used instead of imported Scotch iron. It is made from a mixture of Lake Superior hematites and native black band ores; the average furnace mixture being about 57 per cent. iron. The furnaces are run on a slag containing about 33 per cent. silica and 45 per cent. lime, and the iron varies from 2.75 to 3.75 per cent silicon,—an average of several hundred samples of No. 1 Foundry iron giving 2.92 per cent. silicon. The analysis of good foundry iron has been, with slight variations in silicon, about as follows:

Graphitic carbon	2.95 to 3.25 per cent.
Combined "	.16 " "
Silicon	2.92 " "
Sulphur	.015 " "
Phosphorus	.648 " "
Manganese	.97 " "

The metal is graded according to its appearance on breaking, as follows:

Silvery Iron. A close-grained bright iron, crystals of metal all small. A very weak and brittle iron.

No. 2 Soft. Major part of the surface of fracture shows close-grained bright crystals, with a few larger graphitic plates. A weak iron.

No. 1 Soft. Major part of surface of fracture shows large-grained graphitic crystals. Has numerous close-grained, bright, "mushy" spots. A weak iron.

No. 1 Foundry. Entire surface of fracture shows large-grained, graphitic crystals. A "mild" soft iron.

No. 2 Foundry. Entire surface of fracture shows smaller, darker-grained crystals. A strong iron.

Mill Iron. Very small-grained, dull iron. Very strong and tough.

The lower and colder grades, *viz.*, gray forge, mottled, and white iron, are very seldom made at these furnaces.

A short explanation of the method of judging what grade a cast shall be marked may be of interest. If a No. 1 Foundry iron shows, on breaking, a few close-grained, so-called "mushy" spots of lighter color and smaller crystals than the regular No. 1 fracture and if the crystals appear in these

spots to have partially fused or fritted together the [illegible] be No. 1 Foundry [illegible] on the hot side [illegible] An increase [illegible] ber and size of these spots would cause the iron to [illegible] No. 1 Soft. As the heat received by the metal [illegible] increases the metal shows on fracture a greater [illegible] these mushy spots, the limits of which are however [illegible] defined, but pass imperceptibly into the larger surrounding [illegible] tals. When the greater portion of the fracture exhibits the [illegible] grained bright appearance, the iron is graded as No. 2 Soft [illegible] when the entire surface of fracture is covered with small [illegible] crystals and no large graphitic plates are to be seen the [illegible] ranks as Silvery iron. In passing from No. 1 Foundry [illegible] Mill iron the metal is graded as No. 2 Foundry if the [illegible] fracture are smaller and duller than No. 1 and when [illegible] are very small and dead or dull looking the [illegible] as Mill iron.

The appearance of the crystals on fracture of a [illegible] criterion of the quality of the iron. The terms [illegible] mild, soft, mushy, etc. are local and used [illegible] places with somewhat different meanings. Crystals [illegible] are said to look soft or mild when they are [illegible] nent and very graphitic the color being very [illegible] brilliant. The term sharp or bright is applied [illegible] such as Silvery when the crystals are small [illegible] gray and the luster brilliant. Silvery [illegible] broken almost the color of zinc. [illegible] Foundry and Mill have the crystals [illegible] and of a dull black color.

[illegible]

carbon and silicon than that produced with slower blast, where more time is given for chemical union or physical saturation with these desirable elements.

During the regular working of a furnace an increase in the moisture of the air, a charge of wet ore, or an increased amount of blast will lower the grade of the metal and at the same time lower the percentage of silicon. An increased supply of coke, or a decreased volume of blast, will raise both the grade of iron and the percentage of silicon. This variation of silicon with the grade may be seen from the following consecutive list of analyses. The iron was made on No. 1 furnace on January 19th and 20th, 1890.

DATE.	GRADE.	SILICON.
Jan. 19	No. 2 Foundry	2.36
" 19	Nos. 1 and 2 Foundry	3.18
" 19	No. 1 Foundry	3.21
" 20	" 1 Soft	3.22
" 20	" 2 "	3.92
" 20	" 2 " and Silvery	4.02
" 20	Silvery	4.60

The effect of cooling the furnace in producing Mill iron and lowering the percentage of silicon is shown by the series of casts made January 26th, 1890, and days following:

DATE.	GRADE.	SILICON.
Jan. 26	No. 1 Foundry	2.93
" 26	" 2 Soft	3.86
" 26	" 1 Foundry	3.26
" 26	Mill	*
" 27	Nos. 1 and 2 Foundry	1.74
" 27	" 1 " 2 "	2.03
" 27	" 1 " 2 Soft	3.34
" 27	No. 1 Foundry	3.20
" 28	Mill	*
" 28	No. 1 Foundry	2.90
" 28	" 2 Soft	3.06
" 28	Mill	*
" 29	No. 1 Foundry	2.60
" 29	" 1 "	2.64
" 29	" 1 "	2.85

* Not analyzed.

From the above tables it may be seen that the percentage of silicon increases with the heat of the iron and *vice versa*. While, however, this is practically true, it is not always relatively so. Mill iron is sometimes higher in silicon than good foundry iron made at the same furnace, but this mill iron must have been

cast under unusual conditions. The facts are that in the regular working of a furnace both the grade and the silicon are governed by similar conditions, and circumstances which raise the grade increase the other. There are, however, numerous [illegible] as will hereafter be shown, which affect the silicon or the grade independently of each other.

The rapidity with which iron flows from the tapping hole has considerable influence upon its grade. In order to yield the greatest amount of No. 1 Foundry pig the tap hole should be of sufficient size to permit a rapid flow of iron and the sand runners should be clean and dry. Should the tap be small and the iron flow slowly down the runner and dribble into damp beds the metal becomes chilled, and, in consequence, an iron which at the skimmer shows every indication of heat and under proper conditions would have been good No. 1 Foundry will grade no better than No. 2 Foundry or No. 1 Mill. For this reason the grain of the iron will not always show the amount of silicon it contains. As the furnace is very sensitive when working on [illegible] irons, it often happens that a slight slip of the walls before tapping will lower the grade of the following cast to mill iron without lowering the silicon.

The following series of analyses will show this peculiarity:

Date	Cast No.	Grade	Silicon
May		No. [illegible]	[illegible]
	[illegible]		[illegible]
			[illegible]
		Mill	
		No. [illegible] Foundry	
	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]
		[illegible]	[illegible]

Again, on June 1st a cast of Mill iron contained as much silicon as generally accompanies good Foundry iron.

Date	Cast No.	Grade	Silicon
May	[illegible]	No. [illegible]	[illegible]
June		[illegible]	
		Mill	[illegible]
		No. [illegible] Foundry	[illegible]
	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		No. [illegible] Foundry	
	[illegible]		[illegible]
[illegible]		Mill	
[illegible]	[illegible]	No. [illegible] Foundry	[illegible]

These examples are, however, extraordinary, and serve to show how sensitive the furnace is to any chill when making hot irons, and how readily the grade may change without much alteration in the silicon.

Another peculiarity of high silcon irons must here be noticed. If a very hot iron, high in silicon, be chilled when casting either through a slow run or damp pig beds, the effect is to close the grain and diminish the size of the crystals, thus giving it the appearance of silvery iron. I have frequently noticed such casts of hot iron *chilled to Silvery grade*, and have found the percentage of silicon in such iron is somewhat lower than in the following and preceding casts. Thus:

No.	Furnace No.	Date.	Cast No.	Grade.	Silicon.
7615	2	Aug. 24, '90	3	No. 2 Soft	4.06
7616	2	" 24, '90	4 (slow run)	Silvery	3.69
7617	2	" 25, '90	1 (fast run)	No. 2 Soft	3.88

In analysis No. 7616 I noticed little granules of slag both in the pig and in the drillings. These were easily distinguished from the sand which clings to the pig and is removed by the magnet before analysis. These slag granules suggest a very simple explanation of the lowering of silicon by chill in the runner. Silicon in pig iron has a tendency to brighten the color, because, on account of its avidity for oxygen, it prevents oxidation of the metal during a cast. If, however, a high silicon iron (which cast rapidly should grade No. 1 or No. 2 Soft) be chilled by slow run, an incipient oxidation takes place in the metal. The silica and oxide of iron thus formed unite to form globules of slag which rise out and are entangled in the upper part of the cooling metal. In this way the oxide is removed as fast as formed and the metal is brightened at the expense of a part of the silicon, while the chill closes the grain and gives it the appearance of of Silvery iron.

The percentage of silicon is not, as might be supposed, constant throughout a cast, but varies from top to bottom of the casting house. The first made pig bed at the bottom of the casting floor I have found by several trials lower than the average in silicon, while the bed last filled and nearest to the furnace has higher silicon than the average. A slight change in phosphorus accom-

panies the change in silicon. Two series of analyses are here given which will show this:

Furnace No. [illegible] Sept. [illegible] cast of No. [illegible] iron

	Silicon	Phosphorus
[illegible] pig, bed middle pig	[illegible]	[illegible]
[illegible]	[illegible]	
[illegible]	[illegible]	
[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	
[illegible] *	[illegible]	
[illegible]	[illegible]	
[illegible]	[illegible]	
[illegible]	[illegible]	
[illegible] end of last pig	[illegible]	

* Slag [illegible] about this time

Another set of analyses made October 31st on the following [illegible]

Furnace No. [illegible] A.M. No. [illegible] iron

	Silicon
[illegible] bed middle pig, run slow	[illegible]
[illegible] rapid run	[illegible]
[illegible]	[illegible]

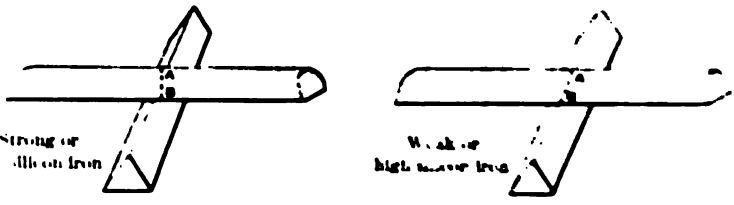
In this case the iron came with a rush after the casting [illegible] was about half full. That which dribbled into the first eight [illegible] was, as shown by the table, lower in silicon than the rest of the cast.

I am aware that some analysts have found at other furnaces a reverse arrangement of silicon to obtain, and the pigs first cast to be higher in silicon than the last. In order to test whether this was the case at Hubbard the above series of analyses [illegible] made, and numerous isolated samples from top and bottom [illegible] cast show that the arrangement here given is or was the rule at these furnaces. The greater percentage of silicon in the pig beds may be due to the fact that silicide of iron is of lower specific gravity than pig iron, and hence tends to rise toward the top of the hearth. It may also be due to the fact that these combinations of iron and silicon, iron and phosphorus, etc., have a higher specific heat than iron alone, and hence cool more slowly. Now, as the cooling iron encroaches more and more from the cast side towards the center, it drives the silicide before it, and as the impurities are concentrated toward the center in a cooling stream. For this reason the center and top of the molten mass in the hearth would contain the greater portion of these impurities, and the iron last running from the furnace would be the richest in silicon. The analyses were purposely taken from casts made from a newly lined furnace in [illegible] condition, and at [illegible]

As the hearth had not been cut away by long use the tap hole was in such position that the iron flowed naturally and did not require blast pressure to force it out. The oxidation of metal by cooling in running down the sand beds may also account in part for low silicon in the first pig. The phosphorus, as will be seen, does not vary so much as silicon. The slight loss of phosphorus in the lowest pig bed may be due to partial oxidation and removal as slag. The average silicon throughout the cast is 2.93 per cent. and the loss on lowest pig bed is 4.4 per cent. of its total amount, while phosphorus is lowered to the amount of only 1.9 per cent. Since the middle pig bed represents most nearly the average silicon in the cast, it has always been my custom where one pig only is taken for drilling to select the middle pig of this bed, and throughout this paper where analysis of a cast is mentioned this pig has been the one selected.

The effect of silicon on pig iron is to weaken the transverse or breaking strength of the metal and to brighten its fracture. This is corroborated by the breakers in the iron yard, to whom a slight increase in the strength of iron is a matter of no small importance. A pig containing 3.5 to 4 per cent. of silicon when dropped from a height of two feet across a triangular block, breaks with almost the ease of glass. The edges of the fracture are clean and sharp, and show no adhering torn fragments. The crystals are brighter and somewhat smaller than in a pig of the same grade but lower in silicon. High silicon iron is likely to break slightly "on the bias," that is, not exactly at right angles to its length. This seems due to the fact that, owing to the extreme weakness of the metal, the fracture follows the direction in which the pig strikes the edge of the block. When strong iron falls across a block in a slightly diagonal direction, the pig breaks across the shortest possible line, *i. e.*, at right angles with its length, as shown in the following cut, the dotted line *AB* being the line of fracture. With a high silicon iron the crystals of graphite set free by the silicon make the metal somewhat softer in texture than low silicon iron, and the edge of the breaking block makes a guiding indentation which the fracture follows even if that be not the shortest possible direction in which the pig could break. Low silicon iron is strong and tough, requiring to be thrown forcibly across

the block from a height, while the fracture is lumpy and [illegible] and numerous torn fragments adhere to the edges of the [illegible].



Silicon appears to act as a softener not by any [illegible] silicon *per se*, but by its effect in causing the greatest possible amount of carbon to assume the graphitic condition. High silicon iron of five to eight per cent. is in itself hard as is also [illegible] with only one-half to one per cent. The hardness in the former case is due to excessive silicon, and in the latter to [illegible] carbon. The high silicon iron when melted with other [illegible] mixtures possesses the property of forcing the carbon [illegible] combined state and allowing it to crystallize in graphite [illegible]. In the manufacture of light castings, stove fixtures [illegible] etc., when the articles are of necessity small and thin [illegible] foundry mixture would chill in the casting and make [illegible] article of white iron. By the judicious admixture of [illegible] this tendency to chill and whiten is overcome, and a [illegible] casting may be made in cases where without the softener [illegible] would be an impossibility.

Since silicon is the element which produces this desirable [illegible] it would seem that a Silvery iron should command a higher [illegible] than No. 1 Foundry. Such however is not the case [illegible] Foundry of three to three and one half per cent. silicon [illegible] ing from a dollar to two dollars per ton more than Silvery [illegible] four to five per cent. Why this should be so is not easy to explain: although foundry men may find some excuse [illegible] that, as their aim is to produce a graphitic casting, the [illegible] No. 1 Foundry iron they employ the more graphitic and soft [illegible] their product. A little reflection would show that the [illegible] of carbon (whether graphitic or combined) in the stock [illegible] is entirely overthrown by the melting in cupolas, and [illegible] silicon in the softener is depended upon to throw the carbon

the casting into the graphitic condition, the more silicon (within certain limits) there is in the mixture, the better will be the results. On this line of reasoning it would evidently be economy to the founder to buy Silvery and No. 2 Foundry iron, both of which can be had cheaper than No. 1 Foundry, and by judicious combination to bring the castings to any percentage of silicon desired. The more scientific way by far would be to base the price of the softening iron upon the percentage of silicon therein.

A few analyses made of various grades of pig iron will show that although silicon changes carbon to the graphitic state, yet, when in excess, it lowers the carbon by actually displacing it from the iron. As these irons varied widely in grade no comparison can be made between the percentage of silicon and that of graphite, other than the fact that both low and high silicon irons are low in graphitic carbon.

No.	Silicon.	Graphite.	Com. Carbon.
6407	1.88	2.86	0.25
6383	2.17	2.85	....
6389	2.50	2.98	0.16
6312	2.36	3.27	....
6399	2.92	3.20	....
6393	3.10	2.98	....
6391	3.75	2.88	....
6395	4.25	2.72	....
5298	5.03	2.67	....

In the high silicon irons there was very little combined carbon and the decrease in graphite is due to actual displacement or crowding out by the silicon. Mr. W. J. Keep, of Detroit, in *Trans. Mining Engineers*, **17**, gives further tables on this subject, showing that in higher silicon irons this element entirely displaces graphitic carbon; one containing 15.38 per cent. silicon having only 0.79 per cent. and one of 23 per cent. silicon absolutely no carbon.

While it is true that high silicon makes brittle pig iron, it does not follow that brittle iron is always high in silicon. During the month of August, 1890, a large amount of soft lake ores, high in phosphorus, which had accumulated in the stock house, were put through the furnace. My attention was very soon called to the weak and brittle nature of the pig iron, and the brilliancy of its fracture. These were almost exactly that of a three per cent. silicon pig iron, while analysis showed it to contain only about one and one-half per cent. Phosphorus, however ran from 0.850

to 0.902 per cent., a fair average analysis showing as follows:

	Per Cent
Graphitic carbon	[illegible]
Combined	[illegible]
Total	[illegible]
Silicon	[illegible]
Sulphur	[illegible]
Phosphorus	[illegible]
Manganese	[illegible]

Since the average phosphorus in Hubbard Scotch is about [illegible] per cent., it is evident that in this case the weakness and brittleness were due to increased phosphorus.

Since, to those not in the habit of handling pig iron, the difference in the physical appearance of irons made at a high or a low heat may not be very evident, it might be well to insert here in tabulated form a list of the main characteristics whereby the two can be distinguished. All other things being equal, hot iron is higher in silicon than cold iron; and by close attention to slight variations in the heat received, and by careful study of the surface indications hereafter described, a skillful observer can form a very shrewd opinion as to the percentage of silicon in any cast.

	Cold Iron		Hot Iron
1	Flows thin in casting	1	Flows thick and [illegible] back while flowing
2	Sparkles slightly in runner	2	Does not sparkle
3	Fills pig beds rapidly		Requires more [illegible] beds
4	Leaves pig beds looking clean and smooth after a cast	4	Leaves pig beds [illegible] and sand
5	If a few beds are sheeted or covered by a rush of iron the sheet sinks into the pig moulds and leaves only a thin connecting tissue of iron	5	If sheeted the [illegible] and sinks into pig moulds [illegible] forms a heavy connecting [illegible] of iron
6	Scrap and scull in runner is thin and light	6	Scrap is thick and heavy
	Sand sticks to pigs	7	Sand does not stick to pigs
8	Crystals small	8	Crystals large grown [illegible] as heat increases
9	Crystals dull, distinct and prominent	9	Crystals bright and smooth [illegible] spots to assume a smooth [illegible] fused appearance
10	Pigs have flat top, rounded at edges to a slight convexity	10	Pigs usually [illegible]
11	Surface blistered and [illegible] containing air bubbles		Surface smooth [illegible] with slight [illegible] pressure [illegible] wrinkled like [illegible] flowing [illegible]
12	Breaks square across with a dull tearing sound	12	Breaks often [illegible] with sharp crack
13	Fracture shows [illegible] adhering		Fracture [illegible] smooth
14	Is tough and strong	14	Is weak and brittle

The surface of [illegible] from [illegible] page [illegible]

As I have said, these are the general physical distinctions between hot and cold iron,—that is, iron above and below a No. 1 Foundry heat. Knowing the general average of silicon produced by a certain mixture of ores—with a given blast and coke supply—these physical differences will serve to give an approximate idea of the amount of silicon.

By far the best criterion of silicon is that afforded by the surface of the pig. On all Hubbard irons over No. 2 Foundry grade I have found certain peculiar markings of surface, which vary with the silicon content and form a standard of reference for it. A high silicon iron, when not roughened by kish or sand, has a smooth and slightly wrinkled or pitted surface, with a continuous skin, nowhere broken, but frequently indented with shallow depressions or pits about the size of wheat grains. This surface is characteristic of medium and high grade irons over 2.5 per cent. silicon. While the surface is very difficult to describe, the appearance can be readily seen by reference to Fig. 1 of the accompanying illustration, No. 1 Foundry iron, silicon, 2.78 per cent. It will be noticed that although the surface is pitted the skin, or outer layer of oxide, is not broken, but flows continuously over all heights and depressions of the surface.

When the silicon is lowered to about 2.5 per cent. a few small angular holes appear, as if around some of the indentations the skin had broken away, leaving a hole about one-eighth inch in depth with jagged and angular edges. These may be seen in Fig. 2; No. 1 Foundry iron, silicon, 2.59 per cent.

As the silicon decreases, the size and number of these spots increase. Fig. 3 shows very plainly the surface of a No. 1 Foundry pig containing 2.15 per cent. silicon. As will be seen, the surface has about one-third of its area covered by these broken and rough spots. The appearance can best be imagined by supposing the original smooth surface to have cracked or peeled away, like a coat of poorly applied paint, showing the rough surface of the iron beneath. Below 1.5 per cent. the iron becomes very rough. The original smooth surface has then almost entirely disappeared, and is represented only by little patches here and there rising like flat-topped toad stools from the rough iron below. The upper surfaces of these "toad stools" are on a level with

each other, and can be readily seen to indicate the original level surface of the molten pig, which on cooling has sunk and shrunk away. Fig. 4 of No. 2 Foundry iron with 1.30 per cent silicon shows this peculiarity. This the breakers term "hacky" — a name aptly descriptive both of the surface appearance and the toughness of the metal. The "sharpness" of low silicon iron as the appearance shown in the illustrations is locally termed, while a valuable criterion of silicon percentage and of machinability in sorting iron, is not applicable to metal colder than No. 2 Foundry. For grades from No. 2 Foundry to Silvery the appearance here described is characteristic and reliable. In fact I have never seen a Hubbard Scotch iron of these grades in which this description did not hold good, and by close attention to the fracture and the surface sharpness I have very frequently given and have seen the shipping clerk give, an opinion on the silicon content which analysis showed within 0.1 or 0.2 per cent of the true amount. In shipping iron direct from the pig bed this method of judgment becomes invaluable, since it frequently happens that a hot cast is made showing every other appearance of high silicon iron but with more or less "sharpness" of surface. If this latter point were not noticed, the iron might be immediately loaded for shipment to a manufacturer who orders a high silicon iron and is very particular to procure it, while if the sharpness of surface is known to be a reliable criterion the iron would be held for analysis before loading on cars.

Below No. 2 Foundry grade the blistered surface due to escape of heat appears and masks the sharpness of low silicon iron. Figs. 5 and 7 show No. 1 Mill pig with its characteristic blistered surface and open holes due to breaking of blisters or air blows. Fig. 6 shows a very cold gray forge iron of 1.45 per cent silicon. The surface of this is deeply marked with blisters and blow holes.

That the sharpness of surface here credited to low silicon is not brought about by other agencies is evident from the fact that although in two years some twenty different compounds were used in the furnace this characteristic always obtained. Moreover the high phosphorus iron mentioned on page 452 possessed every characteristic of high silicon iron except its surface, which was very nearly that shown in Fig. 1, with about one half the [illegible]

covered with sharp, open spots. In high silicon mill irons mentioned on page 456, the surface was smooth and clean, without the blow-holes and blisters usually prevalent. This may be due to high silicon acting as in steel castings, to prevent unsoundness.

I am not aware whether silicon affects the surface of other iron as it does Hubbard Scotch, but would be glad to have the opinions of others on this point. The only claim I make for this as a criterion is that I have found it very reliable on Hubbard Scotch Foundry iron from No. 2 Foundry to Silvery grade and between 1.5 and 3 per cent. silicon.

The question of the state in which silicon exists in pig iron is one that has been often raised but never satisfactorily answered. The reason for the obscurity surrounding this question may be found in the lack of practical value of its solution. Had the difference between graphitic and combined silicon the same metallurgical importance as between graphitic and combined carbon, the question would long since have been answered. It is stated by some metallurgists that silicon in hot irons is both free and combined, and in cold irons it is altogether combined. That silicon in hot irons does not accompany graphite in the form of scales or crystals may be seen from the following test. A large sample of drillings was taken, in which graphitic carbon was 2.98 per cent. and silicon was 2.96 per cent. Now if silicon existed in the same form or manner as graphite, we should expect it to accompany graphite in equal proportions. The sample was shaken in an eighty mesh sieve and the dust passing through found to contain 6.49 per cent. of graphite and 2.87 per cent. of silicon. This proves that silicon does not lie between crystals of pig iron, or coat them, as does graphitic carbon.

I have, however, often noticed that silica which results from the analysis of iron has a certain grain, or crystalline form, resembling the iron analyzed. For example: the silica from a No. 1 Foundry iron appears, when filtered, in large translucent, gelatinous crystals, mixed with scales of graphite, giving the insoluble residue almost the exact appearance, except in color, of the iron from which it was obtained.

In filtering a cold iron, both carbon and silica appear as a slimy black precipitate or residue which usually takes a long time to

burn white. This is especially noticeable where [illegible] driven hard and the iron, while of fair grade lacks the [illegible] and softness which should be present in a good Scotch [illegible] In filtering the residue of such irons the carbon and silica are undistinguishable,—both forming a slimy gray deposit on the casserole. In burning such residues the silica rarely [illegible] burns pure white, but retains a dull gray appearance. Often times crystals or specks of black graphitic color are noticeable which do not yield to prolonged ignition. These do not appear to be carbon, else they would soil the fingers and would ultimately yield to the heat; neither do they appear to be graphitic silica since no surface oxidation is noticeable however the ignition is prolonged. Treatment of the iron with a strong oxidizing agent such as potassium permanganate or bromine after solution will remove these. I am inclined to believe that in these and similar cold irons a combination exists between the combined carbon and part of the silicon, and that this accounts for the gray residue and the graphitic specks noticed on ignition. Moreover the combined carbon and most, if not all, the silicon of cold irons will go into solution in dilute hot nitric acid while the silicon of hot irons remains gelatinous under similar treatment. This would indicate a similarity of the condition of combined silicon and combined carbon. This opinion is also strengthened by the appearance and physical quality of such cold iron. To [illegible] the matter the silicon of hot irons appears to be in the form of an alloy with metallic iron forming a crystalline skeleton around and through which pig iron of high grade forms in its characteristic large crystals each separated from its neighboring one [illegible] by a flake or scale of graphite which is forced from [illegible] the iron by the greater affinity of silicon. This crystalline skeleton of silicon can readily be seen as silicon dissolving the high grade iron and examining the residue which [illegible] masses of silicon [illegible] of the same size and shape as the original crystals of pig iron. In the lower grade colder irons the silicon not being present in sufficient quantity nor the heat of cast being such as to allow a separation of the graphite in large flakes the silicon and part of the carbon appears to remain chemically combined in the interior of the iron crystals. This opinion [illegible]

must state, merely a personal one, on which I would be glad of the advice of others. Mr. Keep, in *Trans. Mining Engineers*, **17**, 700, notes what he considers a combination of silicon and combined carbon in certain castings, and Shimer, Drown, and others in late papers express conviction that in certain irons silicon does not appear to be thoroughly oxidized by the ordinary course of analysis. Could silicon be removed without oxidation from pig iron such problems as its chemical relation and physical condition therein would be readily explained.

SODIUM CYANID AS A COMPONENT OF POTASSIUM CYANID.

By Thos. B. Stillman.

The valuation of potassium cyanid, for commercial purposes, is dependent upon the amount of cyanogen present, the salt being rated from "30 per cent. cyanid" to "98 per cent. cyanid"—the former selling for twenty cents and the latter for sixty cents per pound. The determination of the percentage of cyanogen is usually made by titration with semi-normal silver solution, and in chemical manufactories where potassium cyanid is made, generally constitutes the entire analysis. Potassium cyanid, when pure, contains 40 per cent. of cyanogen; "98 per cent." would, therefore, indicate 39.2 per cent. of cyanogen, and "30 per cent.," 12 per cent. of cyanogen. A sample of the former recently sent me for analysis gave by titration 42.33 per cent. of cyanogen, or a rating of 105.87 per cent. of potassium cyanid. This result immediately showed that another base than potassium was present, and one also whose combining weight was less. Sodium being indicated by qualitative analysis, a quantitative analysis of the sample was necessary to determine the proportions of potassium and sodium combined with the cyanogen.

The method adopted was as follows: The cyanid was weighed, transferred to a platinum capsule, sufficient water added for solution, then dilute sulfuric acid in excess and contents evaporated to dryness and ignition to constant weight. This represented sulfates of potassium and sodium, and after solution in water and acidifying with hydrochloric acid, the sulfuric acid was precipitated and weighed as barium sulfate and calculated to SO_3.

These determinations gave a method of obtaining the proportions of potassium and sodium in the weighed alkaline sulfate as follows:

[illegible] parts K_2O require [illegible] parts SO_3 for K_2SO_4,
[illegible] Na_2O [illegible] SO_3 [illegible] Na_2SO_4.

Let G = weight of sulfate.

x = [illegible] K_2O

y = [illegible] Na_2O

Then $G = x + y + \frac{80}{94}x + \frac{80}{62}y$

or $G = x + y + 0.851x + 0.645y$

$x + y = G - 0.851x - 0.645y$

$0.851x + 0.645y = G - (SO_3 + x)$

$x = \frac{G - (SO_3 + x)}{0.206}$

$y = G - (SO_3 + x)$

Having obtained the values of potassium oxid and sodium oxid, they are calculated to potassium and sodium these weights multiplied by 100 and divided by the weight of cyanid taken the results being the percentages of potassium and sodium respectively in the cyanid. If to these results is added the percentage of cyanogen, as determined by titration with [illegible] silver solution, the analysis is complete.

A sample of the cyanid above mentioned as containing [illegible] as well as potassium gave the following

Amount of salt taken for analysis [illegible] grms.

Weight of [illegible] and alkaline sulfates	[illegible]
$K_2SO_4 + Na_2SO_4$	[illegible]
[illegible]	[illegible]
$BaSO_4$	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

This cyanid of potassium and sodium (though marked potassium cyanide, 98 per cent.) is sold at a lower rate than the 98 per cent. potassium cyanid, and for many purposes is superior, as it contains a higher percentage of cyanogen. An examination of the formula for its manufacture shows that it can be made at a less cost than the potassium cyanid alone. Potassium ferrocyanid, or sodium ferrocyanid, when heated in covered crucibles is converted into potassium or sodium cyanid, iron carbid, and nitrogen;

$$2\ K_4Fe(CN)_6 = 8\ KCN + 2\ FeC_2 + N_4$$
$$2\ NaFe(CN)_6 = 8\ NaCN + 2\ FeC_2 + N_4$$

100 pounds of potassium ferrocyanid, at thirty cents per pound, produces 70.65 pounds of potassium cyanid, 98 per cent., at a cost of forty-two cents per pound; and 100 pounds of sodium ferrocyanid, at twenty cents per pound, produces 64.47 pounds of sodium cyanid, 98 per cent., at a cost of thirty-one cents per pound.

If a mixture composed of 117 pounds of potassium ferrocyanid and 26 pounds of sodium ferrocyanid be heated in covered crucibles, the resulting compound, weighing 100 pounds, will closely approximate, in composition, the sample submitted to me for analysis.

LABORATORY OF ANALYTICAL CHEMISTRY,
STEVENS INSTITUTE OF TECHNOLOGY.

THE VOLUMETRIC DETERMINATION OF COBALT.

BY WILLIAM J. KARSLAKE.

The precipitated potassium cobaltic nitrite is added to a slight excess of caustic soda or potash and boiled until entirely decomposed (until supernatant liquid is colorless) into cobaltic hydroxid and potassium nitrite. To the filtrate $\frac{n}{10}$ potassium permanganate is added, drop by drop, to violet color; then two or three drops of dilute sulfuric acid over and above that necessary to saturate the excess of sodium or potassium hydroxid, and then potassium permanganate in excess, shaking thoroughly during the operation. The dark violet liquid is then strongly acidified with sulfuric acid (concentrated), heated to about 80° C., and the excess of potassium permanganate determined either by

direct titration with $\frac{1}{10}$ oxalate or by adding excess of $\frac{1}{10}$ oxalate and re-titrating the excess with potassium permanganate. This gives the N_2O_3 from which the cobalt may be calculated.

0.501 gms. $K_3Co(NO_2)_6 + H_2O$ gave	with KOH	[illegible]
0.4502	with NaOH	[illegible]
	Theory	[illegible]

As the water of crystallization is not definite and constant, this may be the reason for the lowness of the results.

This is practically Kinnicutt's method for titration of alkaline nitrites. It is supposed that the alkaline solution is sufficiently dilute from the washings before titration.

THE DETERMINATION OF POTASH BY THE METHOD OF LINDO, AS MODIFIED BY GLADDING.

[FROM THE LABORATORY OF BREYER AND SCHWEITZER, [illegible], N. Y.]

Differences in the results of determinations of potash in potash salts caused us to investigate critically the method of Lindo, as modified by Gladding, which is adopted as the official method by the Association of Official Agricultural Chemists. While our results showed differences of one and more per cent. when compared with those obtained by the official method, our results agreed generally well with those obtained by chemists who applied the same method as we did, the method recommended and described by R. Fresenius.

The main difference of the two methods is that the method of Lindo, as modified by Gladding, does not require the conversion of the sulfates into chlorids before the precipitation by chloride of platinum. R. Finkener (*Handbuch der [illegible] von H. Kolbe, 2nd [illegible] von R. Finkener*, 2, [illegible]) recommends a method which permits the estimation of potash directly in the sulfates, provided that only the sulfates of sodium and potassium are present.

Naturally the question arises, whether this may be [illegible] safely in the analysis of potash salts containing other compounds besides the sulfates of potassium and sodium. As to the necessity of removing the sulfates by application of the chlorid of platinum method, we find the following opinions in Fresenius (Quantitative Analysis, 2, [illegible]). The question "is it necessary to precipitate

the sulfuric acid] is denied by Teschemacher and Smith, if, as is the case with saltpeter, only a little sulfuric acid is present and if it is combined with alkali or magnesia. The question is to be answered in the affirmative in the case of the analysis of chlorid and sulfate of potash, where the presence of sulfate of calcium and a great number of other sulfates is to be considered. This has been emphasized by Stohmann, and in case of the presence of a larger amount of sulfates by G. Krause." In order to find the reasons which induced the Association to adopt the method of Lindo, as modified by Gladding, we made a thorough study of the reports of the proceedings of the Association. In Bulletin No. 7 of the Department of Agriculture we find a comprehensive digest of the literature appertaining to the determination of potash up to 1885. In this Bulletin there is described the method which was adopted by the Association of Official Agricultural Chemists at the meeting in Philadelphia, in September, 1884. This method requires the removal of the sulfates. After describing the methods of Stohmann, G. Krause, West, and Ulex, the method of R. R. Tatlock is cited. Then there is given the result of a comparison made by Zuckschwerdt and West of the method of Tatlock and that of Fresenius, the final conclusion being in favor of the latter. "The radical defect of Tatlock's method is found in the solubility of potassium chloroplatinate in solutions of platinic chlorid. In any case the method could only be used successfully in the absence of other acids than hydrochloric acid." An extract of Lindo's paper and method is given without any comment. After a number of extracts from papers of minor interest, the description of comparative experiments executed by Wheeler and Crampton and the recommendations of the Committee on Potash, the full text of Gladding's paper (On the Estimation of Potash) is quoted.

Gladding starts with the surprising statement, that the method of Tatlock is (or was at that time) a strongly advocated modification of the (then) official method, this method having "the great advantage of estimating potash directly, whether in the form of chlorid, sulfate, or nitrate." That this is not the case was shown by Zuckschwerdt and West.*

* Ztschr. anal. Chem., 20, 185.

The statement "Again, it has been found that even when the platinum solution gives, in a blank experiment, a residue perfectly soluble in alcohol, it may, from the presence of certain impurities give results far too high when working with chemically pure chlorid of potassium" is not intelligible. If this should be the case, the determination of potash by chlorid of platinum would be entirely out of the question. But we are not aware that any body except Gladding has made this improbable observation. From these considerations and the alleged difficulty of removing all sulfuric acid, etc., Gladding concludes that "the greater tendency to error is at once evident." That is to say he considers the method of Fresenius as unreliable and troublesome and he would prefer the method of Tatlock if it was not for the one objection that there is a loss varying from 0 to 0.5 per cent. For the same reason ("the labor and great care required to make an accurate potash estimation by the standard method") an examination of the method of Lindo was made. This examination showed that for chemically pure chlorid of potassium Lindo's method gave good results, while for sulfate of potash the results were found to be too high and Gladding suggests "It may be that the presence of free sulfuric acid causes the error." Gladding is evidently led to this belief through Lindo's suggestion that in estimating potash in sulfate of potash in the presence of sufficient hydrochloric acid and chlorid of platinum the reaction

$$K_2SO_4 + 2HCl + PtCl_4 = K_2PtCl_6 + H_2SO_4$$

takes place.

In order to avoid the mistake arising from the presence of free sulfuric acid Gladding recommends an addition of chlorid of sodium and gets by this alteration very satisfactory results as regards accuracy.

The above reaction is not very plausible and the presence of free sulfuric acid ought to be proven before an improvement is based on this assumption. We think that in the presence of sufficient chlorid of platinum the reaction is more likely to take place according to the formula

$$2K_2SO_4 + 2PtCl_4 = 2K_2PtCl_6 + Pt(SO_4)_2$$

This is at least the reaction on which R. Finkener bases his

method of separating sodium and potassium in case these bases are present as sulfates. But even conceding the presence of free sulfuric acid, it is not clear what induces Gladding to believe that this would cause too high results. Lindo's opinion as to this point ought to have been known to him. Lindo says: "If the reaction is complete there will be nothing to remove from the precipitate that alcohol is not capable of dissolving and resort to aqueous fluids in washing is therefore unnecessary. If the reaction is not complete, of course we cannot obtain accurate results, however we may wash, etc., etc." This shows that Lindo was not quite sure about the completeness and nature of the reaction. Moreover, the presence of free acid would tend to lower the results as potassium chloroplatinate is considerably more soluble in alcohol containing free acids than in neutral alcohol. We see from these simple considerations alone that the addition of chlorid of sodium is not necessary, and that the expected effect stands in opposition to the facts. This is further proven clearly by Mr. Winton's paper "On the Use of Sodium Chlorid in the Lindo-Gladding Method of Determining Potash" presented at the meeting of the Association of Official Agricultural Chemists in 1891.

Notwithstanding the evident defects of the method and the very unsatisfactory results obtained, it was adopted as the leading method at the meeting of the Association in 1887.

By looking over the results, obtained by the method and published in the Bulletins of the Department of Agriculture, we see enormous differences, of which the following is an example (Bulletin No. 28, p. 71):

	High.	Low.
1. Kainite	12.73	11.29
2. Cotton-seed meal	2.15	1.33
3. Commercial fertilizer	4.38	3.85
4. High grade fertilizer	4.25	3.67

The figures show the results of the different analyses reduced to the same amount of moisture. As the different analysts found very different percentages of moisture, we have computed in the annexed table the results for dry substance. This lessens the differences somewhat, but still they are large enough to justify the greatest suspicion as to the merits of the method.

TABLE I

Number	Moisture	% potash	% potash in dry substance	Deviation from average
1	9.80	11.81	13.09	0.02
2	9.66	11.81½	13.25	0.14
3	8.69	12.01	13.15	0.04
4	11.72½	11.97½	13.56	0.45
5	8.67	12.75	13.96	0.85
6	9.80	12.33	13.67	0.56
7	9.07	11.76	12.93	0.18
9	9.19	11.31	12.45	0.66
10	10.01	12.06	13.40	0.29
11	6.97	11.54	12.40	0.71
12	9.21	11.72	12.91	0.20
Average				−0.36
	9.15	11.86	13.11	+0.44

TABLE II

Moisture	% potash	% potash in dry substance	Deviation from average
8.28	[illegible]	[illegible]	[illegible]
8.91	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
8.45	[illegible]	[illegible]	[illegible]
8.18	[illegible]	[illegible]	[illegible]
8.44	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
8.18	[illegible]	[illegible]	[illegible]
8.41	[illegible]	[illegible]	[illegible]
8.20	[illegible]	[illegible]	[illegible]
			[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

TABLE III

Number	Moisture	potash	% potash in dry substance	Deviation from average
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Average	[illegible]	[illegible]	[illegible]	[illegible]

TABLE IV

Moisture	% potash	% potash in dry substance	Deviation from average
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

We have made a great number of determinations of potash in potash salts by the official method and by the method of [illegible] so

and we have invariably found great differences in the results. By examining the precipitates obtained, we found that those obtained by the official method generally were contaminated by sulfuric acid, lime, magnesia, and ammonia. We found that in some cases the official method gave higher results, but mostly lower results, notwithstanding the impurity of the precipitate. Especially in salts containing sulfate of magnesium the differences were large; and this observation led us to a thorough investigation of the method.

As the precipitates obtained by the official method contained magnesia, lime, ammonia, and sulfuric acid, and still the results were often found to be too low, we had to find the corresponding amount of potash, which must have been lost in the different operations. For this purpose we examined at first the different washings. We had no difficulty in determining potash in the alcohol washings, but on attempting to determine the potash in the 25 c.c. chlorid of ammonium solution by evaporating the same to dryness and driving off the chlorid of ammonium by ignition, satisfactory results could not be obtained, and the following method had to be employed:—

A quantity of hydrate of barium (7 gms. $Ba(OH)_2$) more than sufficient to expel all the ammonia contained in 25 cc. of a half saturated chlorid of ammonium solution (4.37 gms. NH_4Cl) was added and the liquid boiled until all the ammonia was driven off, then a solution of sulfuric acid was added, which was titrated against the hydrate of barium solution and which was not quite sufficient to precipitate all the barium. By evaporating to dryness on the water-bath, nearly all the chlorin present was driven off as hydrochloric acid. The precipitate of sulfate of barium was repeatedly treated with boiling water, filtered off, and the filtrates were evaporated. The excess of barium and any lime present were precipitated by carbonate of ammonium and oxalate of ammonium. Then the magnesia was eliminated by the oxalic acid process and the resulting carbonates of sodium and potassium were transformed into chlorids and potash was estimated as chloroplatinate of potassium. By this method very small quantities of potash could be determined in the different washings.

The following is an example of an investigation of the results

obtained for a sylvinite by the method of Fresenius and the method of Lindo as modified by Gladding

Method of Fresenius	potash	[illegible] per cent
Lindo-Gladding		[illegible]

The precipitate obtained by Fresenius' method was found to be free from ammonia, lime, magnesia, and sulfuric acid.

500 cc. of the half saturated chlorid of ammonium solution were treated according to the official directions for twenty-four hours with 1.7042 gms. of dry chloroplatinate of potassium which weighed after treatment 1.6187 gms.; dissolved portion was therefore 0.0855 gm. This would indicate that 25 cc. should contain 0.0043 gm. chloroplatinate of potassium, while the direct determination gave 0.0091 gm. By examining the residue of [illegible] gms. for ammonia, it was found to contain ammonia equivalent to 0.0960 chloroplatinate of ammonium. In order to make sure that the ammonia was not due to chlorid of ammonium contained in the residue, another part was carefully washed with absolute alcohol and analyzed for ammonia with the same result as before. Therefore, in the chlorid of ammonium solution there is contained an additional amount of potash, equivalent to [illegible] gm. chloroplatinate of ammonium. This potash is equal to [illegible] gm. chloroplatinate of potassium. 500 cc. of the chlorid of ammonium solution contains, therefore, potash equivalent to [illegible] gm. + 0.1051 gm. = [illegible] gm. chloroplatinate of potassium and 25 cc. contain [illegible] gm. chloroplatinate of potassium.

This agrees very well with the direct determination, and therefore we used for all results the correction of [illegible] gm. chloroplatinate of potassium.

[illegible]

These figures show that by the different washing operations required in the Lindo-Gladding method an amount of potash

equal to 1.46 per cent. is removed from the precipitate, while the difference of the results (15.45 per cent., 14.85 per cent.) is only 0.60 per cent. The balance of the actual loss and the apparent loss must have been made up by impurities in the precipitate of chloroplatinate of potassium. Indeed, the analysis of this precipitate showed that it contained ammonia equivalent to 0.0176 gm. of chloroplatinate of ammonium. This calculated for potash would give 0.0034 gm. of potash, or for 0.5 gm. of substance analyzed 0.68 per cent. The remaining 0.18 per cent. consists of sulfuric acid and magnesia. This thorough examination of the washing liquids was repeated for a number of different commercial potash salts with the same or very similar results. In all cases we found the precipitate of chloroplatinate of potassium contaminated by ammonia and in many cases by sulfuric acid, magnesia, and lime.

From these experiments the following conclusions must be necessarily derived:

1. The addition of chlorid of sodium is unscientific and injurious to the exactness of the results, on account of the enormous amount of alcohol required for washing the precipitate. The wash alcohol generally contained potash. On one occasion 420 cc. of alcohol were used before a colorless filtrate was obtained.

2. The necessity of using such large quantities of wash alcohol in combination with the other wash operations, makes it very doubtful whether the method of Lindo as modified by Gladding is a simplification of Fresenius' method.

3. By washing the precipitate with the prescribed half saturated chlorid of ammonium solution a partial decomposition takes place, chlorid of potassium being washed away, while chloroplatinate of ammonium remains on the filter.

4. The removal of the impurities from the precipitate is not complete, especially in the presence of the sulfates of magnesium and calcium.

5. The method is therefore entirely unreliable; the results are sometimes too high, sometimes too low, according to the amount and quality of the impurities contained in the potash salts.

The sooner this method is abandoned the better for all concerned, for those who buy and sell potash salts and for the chemists who are expected to give satisfactorily agreeing tests.

VOLUMETRIC DETERMINATION OF MERCURY *

By Rod Namias

The volumetric process to be explained is applicable only to mercuric chlorid, into which every other compound must be previously converted. The nitrate must be treated with hydrochloric acid in excess, and evaporated to dryness; the mercurous salts are submitted to evaporation in presence of hydrochloric acid and of potassium chlorate.

The evaporation must be conducted with care at a temperature below that of ebullition, so as to avoid any loss of mercuric chlorid by volatilization.

The process depends upon the following principle It to a solution of mercuric chlorid, slightly acidified with hydrochloric acid, we add a solution of stannous chlorid, the mercuric chlorid is reduced first to the mercurous state and then to metallic mercury. But whilst the first reaction is nearly instantaneous, the second takes a longer or shorter time, so much the longer as the excess of the stannous chlorid is less

If we have a reagent by which we can recognize the moment when the stannous chlorid is in excess for the first reaction and begins to produce the second, we may by this means determine the mercury volumetrically.

The reagent for detecting the presence of stannous chlorid in excess is sodium molybdate I dissolve a small quantity of molybdic anhydrid in a solution of sodium hydroxid or carbonate I steep in this liquid a morsel of filter paper which I spread out whilst wet upon a plate of porcelain The solution of molybdate ought to be freshly prepared, and the paper of good quality it must not take a yellow tint on immersion in the alkaline liquid The paper must be steeped in the molybdate only a little time before the experiment so that it may not have time to dry

The paper thus prepared shows a relatively slight excess of stannous chlorid which communicates to it according to its quantity a color varying from the lightest sky blue to an intense blue This color is due to the reduction of the molybdic acid

* Chem. News from Rev. de la Société des Mines

Ammonium molybdate, less stable than sodium molybdate, is less fit for use.

The determination of the value of the stannous solution may be made by means of a standard solution of iodin; but it is preferably effected by operating upon a known quantity of pure mercuric chlorid obtained by sublimation.

If we operate with iodin we obtain a slight error in excess due to the small quantity of stannous chlorid, which must be used in excess to mark the end of the operation by spotting upon the molybdate paper. In any case it is well to determine the standard of the stannous solution by means of iodin approximately, if not exactly; this serves as a control, and facilitates at the same time the exact titration by means of mercuric chlorid.

To prepare the solution of stannous chlorid I dissolve 2 to 3 gms. tin by means of hydrochloric acid, and dilute it to 1 liter. This solution is preserved in an apparatus which prevents alteration by contact with air. I determine its strength as follows:—0.2 to 0.4 gms. of mercuric chlorid weighed exactly are dissolved in 50 cc. of distilled water, and acidulated with ½ cc. of concentrated hydrochloric acid. Into this cold solution the stannous solution is allowed to flow from a burette. If the detemination of the standard has been previously made with iodin, we may pour in at once, without fear of overstepping the limit, the volume is determined by calculation from the titration with iodin; we then add the liquid drop by drop, stirring carefully, and each time putting a drop of the mixture with the stirring-rod upon the molybdate paper. An excess of a few drops of the stannous liquid turns the paper to a pale blue, which becomes manifest after a few seconds, and which an experienced eye easily recognizes.

To obtain a well marked coloration, it is necessary to use an excess of from 0.3 to 0.5 cc. for 50 cc. of liquid. The small quantity of mercurous chlorid placed upon the molybdate paper whilst "spotting" has no injurious influence upon the result.

The proportion of free hydrochloric acid contained in the liquid should be about 0.5 cc. to 50 cc. of the liquid; a larger proportion may occasion errors from its action upon the molybdic acid in presence of filter paper.

To obtain exact results we must operate each time exactly as when standardizing the liquid. We must as far as possible operate upon the same volume of liquid, in presence of the same proportion of hydrochloric acid, and obtain spots of the same intensity upon the molybdate paper.

NOTE ON MILK ANALYSIS

By Dr. Russell Davenport

To restore to the emulsion any small quantity of butter fat which may have become churned out in a sample of sweet milk which is to be analysed, I have usually found the addition of about one per cent., by volume, of ether, and a good shaking up of the sample, to be all that was needed. The diminution in the weight of the results of the analysis caused by this dilution of the sample by the ether is too small to call for any correction, being well within the usual limits of variation from manipulation. It is simple enough, however, to allow for it. I report this simple device, never having seen it recommended.

Map of Normal Waters of New York State. Prof. M. P. Mason, of Troy, N. Y., writes as follows to the Editor: I would be obliged if you would mention the fact that I am individually at work upon a map of normal (or unpolluted) waters of the state of New York, and would be glad to receive assistance in the shape of copies of already existing analyses of such waters, with geographical and local descriptions, etc. My object is to eventually so map the state as to be able to say how a surface hill rain or spring water should commonly run in any given locality. As you know, Massachusetts has some such map for chlorin

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STANDARD IODIN SOLUTION: A METHOD FOR ITS PREPARATION.

BY H. L. PAYNE.

Of the methods proposed for determining sulfur in iron and steel, that first suggested by Elliott (*Chemical News*, **23**, 61) merits attention on account of the ease and celerity of manipulation, as well as accuracy of results obtained. This last point has been held in question by many chemists, but the record obtained by Lee S. Clymer, of the Crane Iron Co. (see this Journal for June, 1892) places it on a par with those longer methods which have been considered highly accurate.

The essential feature of Elliott's method is the titration of the sulfur evolved as hydrogen sulfid, with a standard solution of iodin. Several methods are in use for the preparation of this solution of iodin.

The one given in Blair is tedious, in that it involves the use of two other standard solutions, one of potassium bichromate, and another of sodium thiosulfate, as well as an indicator solution of starch; moreover, the use of ammonium carbonate to retard the decomposition of the thiosulfate introduces a serious error in the titration, as has been pointed out by Topf (*Ztschr. anal. Chem.*, 1887, p. 137).

Mohr's method by weighing clear crystals of thiosulfate and Fresenius' method by re-subliming and weighing the iodin direct, are both shorter and better.

A solution may also be made sufficiently exact for most uses by weighing four gms. iodin to the liter where five gms. of iron are taken for analysis, but like all the above methods, it involves an uncertain error.

We have used for some time the following method and find it eminently satisfactory in every way. It depends upon the reaction between potassium permanganate and potassium iodid in solution:

$$K_2Mn_2O_8 + 10KI = 10I + 2MnO + 6K_2O$$

Sufficient acid, preferably sulfuric, is added to keep the manganese in solution and to render the fluid slightly acid. This reaction takes place in the cold and proceeds to completion even in dilute solutions. The strength of the permanganate solution being known, we can readily determine the amount of iodin liberated. One equivalent of potassium permanganate liberates ten atoms of iodin, or oxidizes ten atoms of iron. Hence one atom of iron corresponds to one atom of iodin, and as one atom of sulfur reacts with two atoms of iodin, two atoms of iron equal one atom of sulfur; or 128 gms. iron are equivalent to thirty two gms. sulfur. Therefore, the sulfur value of our permanganate solution will be $\frac{32}{128}$ or one-fourth of its iron value.

In preparing a standard iodin solution by this method, we are accustomed to proceed as follows:—

Take about ten gms. potassium iodid in a liter flask, add ten to fifteen cc. dilute sulfuric acid, and run in the calculated amount of potassium permanganate solution from a burette. Agitate a few moments until the reaction is complete and the solution clears, and dilute to the mark with water. A liter of such a solution can be prepared inside of two minutes in any laboratory having a standard permanganate solution constantly on hand, and there is, therefore, no necessity for keeping a standard iodin solution long enough to have it change materially.

A solution of permanganate such as is used in Emmerton's method for phosphorus titrates 6.141 gms. iron per liter, and of such a solution 325.7 cc. will make one liter of iodin solution titrating 0.01 per cent. sulfur per cc. on five gms. iron or steel taken.

As an absorbent for the hydrogen sulfid common white potash is to be preferred; potash purified by alcohol should be avoided. Dilute sulfuric acid may be used with advantage in acidifying the potash solution. The addition of methyl orange to the starch solution in sufficient quantity to give a perceptible red color so

the solution to be titrated, will by turning colorless or a faint yellow on acidifying indicate when an excess of acid has been added.

WASHINGTON, D. C., SEPT. 1892.

RAPID DETERMINATION OF PHOSPHORUS IN IRON ORES.

BY FRANK L. CROBAUGH.

The method described below for the determination of phosphorus in ores, though very familiar in principle, yet contains some details I have not seen published elsewhere.

The results obtained by its use agree closely with those of the magnesia method conducted with much care, and are obtained in a short time.

METHOD.

To five grams of the ore in a round bottom six inch evaporating dish, add sixty cc. of hydrochloric acid, specific gravity 1.20. Cover and place on a tripod carrying a piece of asbestos board about seven inches square and one-quarter of an inch thick; through the center is cut a circular hole two inches in diameter, in which the bottom of the dish may rest. Apply the full heat of a Bunsen burner to the bottom of the dish. The upper edges of the dish will be kept cool and condense the steam formed, thus washing down a crust that would ordinarily form, an especial difficulty when evaporating with nitric acid. Solution of the ore and evaporation in the covered dish to a volume not exceeding fifteen cc. may be accomplished within twenty minutes.

At this point lower the flame, push the glass aside, and add thirty-five cc. of nitric acid, specific gravity 1.42. Push the glass into position and again evaporate at a strong heat to about fifteen cc. During both evaporations it is well to have a stout wire twisted into a fork, whereby the dish may be lifted and its contents given an occasional whirl about the circumference. At the end of the second evaporation only traces of hydrochloric acid will remain, and do not interfere with the precipitation of phosphoric acid. Dilute the solution in the dish to about thirty-five cc., filter while still hot into a shaking flask at the pump.

Place residue and filter at once into a platinum crucible and ignite over a blast lamp. Cool by aid of the blast, add sodium carbonate and fuse to perfect fluidity over the blast lamp. Allow the cold blast to play for a moment on the crucible, then plunge the crucible and contents into about twenty-five cc. of nitric acid 1.135 specific gravity, previously added to the dish in which the original solution was effected. Cover the dish and heat to boiling. The fusion will dissolve with great readiness in this acid. Another paper has in the mean time been placed in the funnel over the shaking flask, and there the residue is filtered into the original solution. All operations, including the filtration of the residue, will not require over forty-five minutes. The total solution and washings need not exceed 150 cc.

Heat the combined filtrates to 90° C., add at once seventy-five cc. of molybdate solution (Dr. Drown's formula), causing mixture by whirling a moment before placing the stopper in the flask. Shake violently about five minutes. Filter at pump on Munktell's No. 0, nine cm., paper. Wash with two per cent sulfuric acid, specific gravity 1.84, as recommended by Mr. Jones.

If reduction is to be effected by mossy zinc in a flask much time is saved by using a bit of absorbent cotton in the neck of a short stem funnel to filter off the excess of zinc, instead of the plaited filter recommended by Mr. Emmerton. The cotton yields no oxidizable material.

By the above course of procedure and titration with potassium permanganate I obtained the results given below in one hour and a half, average time. By treating the yellow precipitate by Mr. Handy's method, or by use of the Jones reductor the time required would have been less.

	Phosphorus	
	Molybdate	Volumetric
Analysis: Hematite [illegible]	[illegible]	[illegible]
	[illegible]	[illegible]
Standard Alloy [illegible]		[illegible]
		[illegible]
[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]
	[illegible]	[illegible]
	[illegible]	[illegible]
	[illegible]	[illegible]
	[illegible]	[illegible]

The Angeline hematite held, on an average, 0.008 per cent. phosphorus in its residue.

About six months ago I obtained equally good results in a variety of ores by this method, but not expecting to use them again, did not make record of the same.

LABORATORY OF STEWART IRON CO.,
SHARON, PA.

FORD'S MULTIPLE STIRRING AND FILTERING APPARATUS.*

Mr. S. A. Ford, chemist to the Edgar Thomson Steel Works, has designed and had in successful and practical use for some time, an ingenious apparatus for stirring, pouring, and filtering a number of solutions at one operation. It is intended more particularly for phosphorus determinations but may also be used to great advantage at superphosphate works or in any laboratory where there are a number of similar determinations to be made daily.

The beakers or flasks are heated uniformly by means of ten argand burners; the holders for the dishes, flasks, and, beakers are so arranged that they may be placed in position very quickly and then emptied upon the filters by one movement.

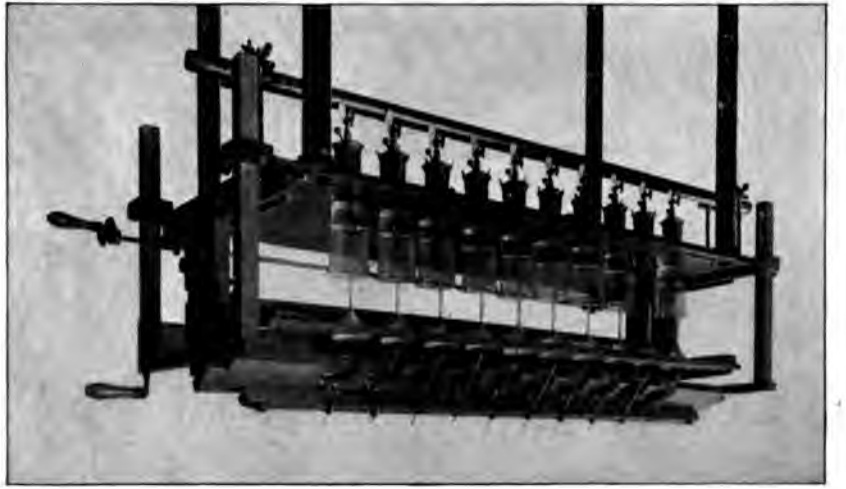
By use of the stirring arrangement all the beakers are stirred at the same time, and the precipitate comes quickly in a coarse, granular condition which never passes through the filters.

The good effect of the stirring is particularly noticeable in the molybdic method for phosphorus. With five minutes stirring all the phosphorus is precipitated, whether 0.03 per cent, or 3.00 per cent. be present.

As the stirring rods never touch the sides of the beakers the precipitate does not adhere to the beakers and is readily washed out. By aid of the machine from forty to fifty determinations can be made in a day by one person. The directions for the use of the machine read as follows:

*This description was furnished at our request by Mr. John G. Bullock of the firm of Bullock and Crenshaw. He has also kindly sent the electrotype from which the illustration has been printed. Mr. Ford writes to the Editor as follows concerning the working of the apparatus: "I will simply say I am delighted with this machine. One young man can make fifty determinations with it between the hours of nine A. M. and three P. M."

"To make phosphorus determinations in iron or steel by the aid of this apparatus where Dr. Drown's dilute acid is used weigh the samples, put them in eight ounce Erlenmeyer flasks pour on the acid, and place the flasks over the lights until solution is complete. The flasks are then caught around the necks by the apparatus designed for that purpose. They are all removed from the lights together and in their places the beakers to be used for the precipitation of the phosphorus are placed with about one-quarter of an inch of water in them, as the lights are still burning. The funnel rack is then brought down and each funnel will go into its separate beaker; filters are placed in position. The apparatus holding the flasks is then placed on the support above and back of the funnel rack. The flasks are gradually tipped and their solutions poured into the funnels. The flasks are then washed out and removed, the filters washed and the funnel rack thrown up out of the way. The lights are now turned up and the solutions heated nearly to boiling. Now oxidize this solution by the permanganate and redissolve the excess of manganese. Lights are now turned out and the ammonia added, and the precipitate caused by the ammonia is redissolved. Thermometers are placed in the beakers and when the solutions are cooled to the desired temperature the thermometers are removed and the molybdic solution added. By means of the crank at the back of the apparatus the stirring arrangement is brought directly over the beakers. The rods used are provided with small rubber corks. Place the rods in the small holes in the stirring bar and press the corks into position, thus holding the rods straight and firm. The crank at the top of the apparatus is then turned for about five minutes, thus causing the rods in the beakers to rotate. With five minutes stirring all the phosphorus will be precipitated. The rods then are taken from the stirring bar and placed in their several beakers. The stirring arrangement is then run back to its former position by the same means which brought it forward. Now place the apparatus for holding the beakers on the upper support, the same used for the flask holders. The beakers are then placed in the several holes in this apparatus with their lips towards the front. When the beakers are all in position the small wooden



bar, with notches on the upper side and small pieces of rubber on the lower, is fastened down by means of the thumb-screws found near the ends of the beaker holder. Now place the rods in the notches in a slanting position so as to touch the lips of the beakers.

"Remove the apparatus containing the beakers from its support for an instant, and bring down the funnel rack. Place filters and beakers in position to receive the filtrate and return the apparatus containing beakers to its former position, just back and above the funnel rack. Now draw the beakers close to the funnel rack, and gradually tip all and pour their contents into the filters.

"When all the solutions are out of the beakers wash and return to a perpendicular position. Wash the filters thoroughly. If the yellow precipitate is to be dissolved, remove the rods from their several notches and wash off with a little dilute ammonia.

"The filtrates are removed from beneath the funnels, and in their places are put the vessels intended to receive the dissolved yellow precipitate. The beakers containing the washing from the rods are now tipped over the funnels again and washed out with a little dilute ammonia. The amount of ammonia here used will, in most cases, dissolve the precipitate in the filters. Use more if necessary, and in either case the filters are afterwards washed with water, and the solution of the yellow precipitate is then ready either for reduction or re-precipitation.

"If the yellow precipitate is to be weighed, the rods and beakers may be rubbed off by means of a glass rod with a piece of rubber tubing on the end."

The machine is manufactured and sold by Bullock and Crenshaw, Philadelphia.

NOTE ON THE DETECTION OF CHLORIN AND BROMIN IN PRESENCE OF IODIN.*

By D. S. Macnair. Ph.D., B.Sc. (Lond.).

When freshly precipitated moist silver iodid is heated with potassium bichromate and concentrated sulfuric acid, no iodin is set free, but the precipitate readily dissolves, forming silver

* Chem. News. 66, 5.

iodate, which is precipitated, along with some silver bichromate on diluting moderately and cooling the solution. Silver bromid when treated in the same way, gives silver sulfate—the whole of the bromin being set free; while silver chlorid behaves like the bromid, giving free chlorin and silver sulfate.

These reactions furnish an easy method of detecting chlorids or bromids in presence of iodids. It is only necessary to precipitate with excess of silver nitrate, filter off and wash the precipitate, and heat it with powdered potassium bichromate and a little strong sulfuric acid. If any chlorid or bromid is present even with a very large excess of iodid, its presence is easily detected by the evolution of chlorin or bromin.

I am at present making further experiments with a view to determining the delicacy of the reaction and also whether it can be conveniently employed for the quantitative separation of iodin from chlorin and bromin.

REPORT ON THE TECHNICAL DETERMINATION OF ZINC.*

In accordance with the plan outlined some time since your committee appointed for the purpose has undertaken the work of attempting to establish a uniformity in the technical methods of analyses in the West, and as the result of its first effort it begs with presents to your body the work of a number of our best known western chemists on zinc determination

It may be remarked that the samples of ore on which the work was done were such as seemed to offer the greatest difficulty in the correct determination of the metal in question

The ores so submitted were from a number of mines of widely separated localities, they were mixtures of galenite pyrite and sphalerite accompanied by greater or less percentages of manganese in the form of rhodochrosite associated with a quartz or gangue

That a standard of comparison might be had by which the various results could be judged, the assistance of the chemists

* [illegible]

laboratory of the U. S. Geological Survey at Washington, D. C., was invoked. Mr. F. W. Clarke, Chief Chemist of the Survey, notwithstanding the fact that his department is always busily engaged with work correlated to the geological investigations of the Survey, met our request for the co-operation of his laboratory in the work to be undertaken with the greatest willingness, and your committee takes this occasion to express its deep appreciation of the valued assistance thus afforded.

The analyses were made by Mr. L. G. Eakins, one of the ablest of Mr. Clarke's corps of chemists, and your committee does not doubt that the results furnished by him will unhesitatingly be accepted as standard by all the technical chemists who assisted in the investigations.

The samples of ore distributed came from the following mines:

Enterprise Mine, at Rico, Colorado.

Mary Murphy Mine, near St. Elmo, Colorado.

Robinson Mine, Robinson, Colorado.

New York Mine, near Park, Colorado.

Moyer Mine, Leadville, Colorado,—the ore from this property being a concentrate product.

These were designated, respectively, Nos. 5, 9, 11, 13, and 20, great care being taken in the mixing of each separate large sample, so that uniformity in the material subsequently distributed might be assured.

The analytical methods employed by the different chemists are given, together with the results obtained. In one instance, that of Dr. H. C. Hahn, in conjunction with the zinc determination, that of manganese is also furnished, thus happily affording a knowledge of the extent to which the latter element was present.

Method of L. G. Eakins, Chemist U. S. Geological Survey, Washington, D. C.—About one gram of ore was treated with twenty-five cc. of dilute hydrochloric acid (1 : 1) and after digestion on the water bath three cc. of nitric acid were added, the whole being then evaporated to dryness. The dried mass was digested with dilute hydrochloric acid and water, and the insoluble residue filtered off. The filtrate was precipitated with hydrogen sulfid, filtered, and the precipitate re-dissolved in nitro-

hydrochloric acid, evaporated nearly to dryness, and water and hydrochloric acid added.

This solution was once more precipitated with hydrogen sulfid the precipitate filtered off, washed, and the filtrate combined with the first. The solution was now oxidized with nitric acid and a basic acetate precipitation made. The resulting precipitate was filtered off, dissolved in dilute hydrochloric acid and re-precipitated as basic acetate, filtered, and this precipitate again dissolved. This solution was evaporated to expel excess of acid, and then poured with constant stirring into an excess of strong, cold ammonia, the precipitate allowed to stand for some time, after which it was filtered off and washed.

The solution from the last ammonia precipitation was found in every case to still contain zinc which had not been removed by the two previous basic acetate precipitations, the amount so held varying from 0.30 per cent. to 2 per cent.

The filtrates from the basic acetate precipitations were combined, evaporated to a convenient bulk, about five grams of acetate of sodium and five cc. of glacial acetic acid added the solution heated to boiling, and the zinc precipitated with hydrogen sulfid. The precipitated sulfid was allowed to settle the solution filtered, and the precipitate washed with hydrogen sulfid water containing acetate of sodium.

The filtrate obtained from the ammonia precipitate was now evaporated to expel excess of ammonia, acetate of sodium and glacial acetic acid added, and the zinc precipitated as sulfid in the same way as has just been described.

The zinc sulfid precipitates were combined and digested with dilute hydrochloric acid containing hydrogen sulfid. All arsenic and traces of nickel (if present) were left undissolved the zinc and any cadmium that might be present passing into solution. This solution was filtered, the filtrate evaporated to expel the hydrogen sulfid and the zinc precipitated as carbonate with carbonate of sodium in the usual way, being finally weighed as oxid of zinc.

This was dissolved in dilute hydrochloric acid the small amount of silica which may have contaminated the precipitate filtered off, washed, and weighed.

To the filtrate an excess of tartaric acid was added, then an excess of caustic soda, and after the solution was diluted to a large bulk it was boiled in a platinum dish to precipitate any cadmium which might have been associated with the oxid of zinc. The precipitate so obtained was filtered off, washed, and weighed, and correction made for such amount, together with what silica had previously been found.

The results were as follows:

No. 5	14.64	per cent. zinc.
" 9	24.11	" " "
" 11	10.71	" " "
" 13	6.31	" " "
" 20	16.09	" " "

Note: Sample number five contained appreciable quantities of cadmium, sample number nine very small quantities, and the other samples only traces of this element.

Method of Messrs. von Schulz and Low, Chemists and Assayers, Denver, Colorado.—Prepare a solution of ferrocyanid of potassium by dissolving forty-four grams of the pure salt in distilled water and diluting to one liter. Standardize as follows:

Dissolve exactly 200 milligrams of pure oxid of zinc in a beaker in ten cc. of strong pure hydrochloric acid. Now add seven grams of C. P. chlorid of ammonium, (the commercial article frequently contains a little copper), and about 100 cc. of boiling hot water. Titrate the clear liquid with the ferrocyanid solution until a drop, when tested on a porcelain plate with a drop of a strong aqueous solution of acetate of uranium, shows a brown tinge. About sixteen cc. of ferrocyanid will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing after each additional drop of ferrocyanid. As soon as a brown tinge is obtained note the reading of the burette, and then wait a minute or two and observe if one or more of the previous tests do not also develop a brown tinge. Usually the end-point will be found to have been passed by a test or two and the proper correction must then be applied to the burette reading. Finally make a further deduction from the burette reading of the amount of ferrocyanid required to produce a brown tinge under the same conditions when no zinc is present. This correction is about two drops, or 0.14 cc.

Two hundred milligrams of oxid of zinc contain 160.4 milligrams of zinc, and one cc. of the above standardized solution will equal about 0.01 gram of zinc, or about one per cent when one gram of ore is taken for assay.

Prepare the following solutions for the assay of ores:

A saturated solution of chlorate of potassium in nitric acid made by shaking an excess of the crystals with the strong pure acid in a flask. Keep the solution in an open flask.

A dilute solution of chlorid of ammonium containing about ten grams to the liter. For use heat to boiling in a wash bottle.

A wash bottle of hot water.

Take exactly one gram of the ore and treat in a 3½ inch casserole with twenty-five cc. of the above chlorate solution. Do not cover the casserole at first, but warm gently until any violent action is over and greenish vapors have ceased to come off. Then cover with a watch-glass and boil rapidly to complete dryness, but avoid overheating and baking. A drop of nitric acid adhering to the cover does no harm. Cool sufficiently and add seven grams of chlorid of ammonium, fifteen cc. of strong ammonia water, and twenty-five cc. of hot water. Boil the covered mixture one minute and then, with a rubber tipped glass rod, see that all solid matter on the cover, sides and bottom of casserole is either dissolved or disintegrated. Filter into a beaker and wash several times with the hot chlorid of ammonium solution. A blue-colored filtrate indicates the presence of copper. In that case add twenty-five cc. of strong pure hydrochloric acid and about forty grams of granulated test-lead. Stir the lead about in the beaker until the liquid has become perfectly colorless and then a little longer to make sure that the copper is all precipitated. The solution, which should still be quite hot, is now ready for titration. In the absence of copper the lead is omitted and only the acid added. About one-third of the solution is now set aside and the main portion is titrated rapidly with the ferrocyanid until the end point is passed, using the uranium indicator as in the standardization. The greater part of the reserved portion is now added and the titration continued with more caution until the end point is again passed. Then add the remainder of the reserved portion and finish the titration care-

fully, ordinarily by additions of two drops of ferrocyanid at a time. Make corrections of the final reading of the burette precisely as in the standardization.

Gold, silver, lead, copper, iron, manganese, and the ordinary constituents of ores do not interfere with the above scheme. Cadmium behaves like zinc. When known to be present it may be removed, together with the copper, by the proper treatment with hydrogen sulfid, and the titration for zinc may be made upon the properly acidified filtrate without the removal of the excess of gas. There seems to be no simpler way to remove cadmium.

The following results were obtained on the samples of ore sent us by the Colorado Scientific Society. Each sample was assayed only once. The weighing was done on the ordinary ore-scale and the burette used had not been corrected. It was intended to show just what would be obtained by the method in ordinary technical work.

Sample No.	5	15.31	per	cent.	zinc.
" "	9	24.34	"	"	"
" "	11	10.76	"	"	"
" "	13	6.42	"	"	"
" "	20	16.14	"	"	"

Notes on the above scheme:

Acids destroy the delicacy of the uranium test, and for this reason a strong aqueous solution of uranium acetate is used. By having the zinc solution only faintly acid the production of the brown color in the end test becomes almost instantaneous and no previous test will develop a color. Under these conditions, however, lead is apt to seriously interfere and the excess of acid recommended above is found to be a necessity. When a strong solution of uranium acetate, not acidified, is used as indicator, the error caused by the excess of acid in the zinc solution amounts to only two drops of ferrocyanid, which may be allowed for, and the brown tinge develops so rapidly that the end point is seldom passed by more than one test.

When an ore contains but little copper, the granulated lead used frequently coheres in lumps that may hold zinc solution. These lumps are most easily broken up after a little of the ferrocyanid has been added. They appear to cause no appreciable

error in the work. Of course, lead shot or thin sheet lead may be used if preferred, and it may be cleaned with strong nitric acid and used repeatedly. It seems simpler and more satisfactory, however, to use the granulated lead and throw it away after use.

As regards the effect of nitric acid, it is found that the addition of one cc. of the strong acid to the boiling hot zinc solution during the standardization of the ferrocyanid makes no appreciable difference.

Method of Mr. L. W. W. Jones, Chemist Pueblo Smelting and Refining Company, Pueblo, Colorado.—The method used was that published some time since by Messrs. von Schulz and Low, Chemists and Assayers, Denver, Colorado, which consists in effecting a decomposition of the ore by means of concentrated nitric acid saturated with chlorate of potassium, evaporating to dryness, and bringing the zinc into solution by means of water, ammonia water, and chlorid of ammonium; heating the solution to boiling, filtering off the insoluble residue, and washing. If the filtrate shows the presence of copper, this metal is precipitated after acidifying the solution with hydrochloric acid by means of granulated lead.

To the hot solution a few grams of sulfite of sodium are now added to counteract any effects due to the possible presence of free chlorin from the action of the hydrochloric acid on any chlorate that might not have been decomposed, and the zinc titrated with a standardized solution of ferrocyanid of potassium using acetate of uranium as an indicator.

The readings of the burette were corrected by an amount of ferrocyanid necessary to produce a reaction with acetate of uranium in a blank test, the standardization having been made under like conditions.

The results obtained on the samples submitted were

[illegible]

Method of Mr. J. N. Hawkins, Superintendent Hilarion Smelting and Refining Company, Leadville, Colorado.—One gram of ore is treated in a [illegible] inch casserole with five to ten cc. of [illegible]

centrated nitric acid, evaporated to dryness on a hot plate and baked for several minutes. After cooling, twenty to thirty cc. of water are added, and about seven grams of chlorid of ammonium and fifteen cc. of strong ammonia water.

If the ore is free from manganese proceed as follows:

Boil for several minutes, filter and wash with warm water, taking the precaution to add a few drops of ammonia water to the first wash water on filter to keep the zinc in solution. It is more convenient to operate in this way than to use ammoniacal wash water.

Neutralize the filtrate with hydrochloric acid, then add an excess of ten cc. of the acid. If copper is present precipitate it with granulated lead.

The solution is now ready for titration with ferrocyanid of potassium, uranium acetate being used as an indicator.

If manganese is present, after addition of chlorid of ammonium and ammonia water as stated above, add to the solution five cc. of peroxid of hydrogen and boil. The manganese will all be precipitated as the hydrated dioxid together with such iron and alumina as may be present. Filter, using the regular precautions.

Now dissolve the precipitate in a small quantity of hydrochloric acid, dilute with water, add an excess of ammonia water and again five cc. of peroxid of hydrogen, boil for several minutes, filter and wash, and combine filtrate with the one previously obtained.

The solution is now made acid with an excess of hydrochloric acid, and the titration of the zinc effected, after removal of any copper that may be present, as previously specified.

In ordinary practice it has been found that the amount of zinc which is carried down with the manganese in its first precipitation by means of peroxid of hydrogen, in the ores which carry from three to ten per cent. of that element, is equal to about five per cent. of the total quantity of zinc present, although this does and will vary somewhat with different practice and the amounts of reagents employed.

The results obtained were as follows:

No. 5	15.66	per cent. zinc.
" 9	24.23	" " "
" 11	11.88	" " "
" 13	8.73	" " "
" 20	15.86	" " "

Method of Mr. F. C. Knight, F.C.S., Chemist Boston and Colorado Smelting Company, Argo, Colorado.—One gram of ore is taken and mixed in a 3½ inch casserole with ten grams of nitrate of ammonium and ten cc. of concentrated nitric acid added. The casserole is covered with a watch-glass and the mixture evaporated to complete dryness on a hot plate. The mass usually deflagrates just before becoming completely dry.

After cooling, about twenty cc. of water and five grams of chlorid of ammonium are added.

If manganese is present, of which previous indication will have been afforded, add to the solution five cc. of peroxid of hydrogen and ten cc. strong ammonia water, heat to boiling for two or three minutes, filter and wash with water containing ammonia water.

As the precipitate of iron and manganese carries zinc it is redissolved in a small quantity of hydrochloric acid, water and chlorid of ammonium added, then five cc. peroxid of hydrogen and ten cc. ammonia water as before. Boil, filter and wash with hot water rendered ammoniacal, and combine the two filtrates. The second precipitation of the iron and manganese practically brings all zinc into solution.

The filtrate should now measure from 250 to 300 cc. It is slightly acidified with hydrochloric acid and if copper is present it is precipitated with granulated lead.

To the solution now add an excess of ten cc. hydrochloric acid and titrate the zinc with a standardized solution of ferrocyanid of potassium, one cc. of which is equal to about five mgms. or 0.50 per cent. zinc. Acetate of uranium is used as an indicator of final reaction.

As about five to six drops of the ferrocyanid solution will be absorbed in a blank test before the reaction with acetate of uranium manifests itself, due allowance must be made for this error in the standardization of the solution. It is almost needless to remark that a similar precaution must be observed in taking the reading of the burette in the actual titration of the zinc solution of the ore. Results obtained were as follows:

[illegible]

Method of Mr. Mann Page, Chemist Omaha and Grant Smelting Company, Denver, Colorado.—The ore is decomposed by boiling in a casserole with a mixture of concentrated hydrochloric, nitric, and sulfuric acids, added separately in the order given, the amounts of acid varying according to the demands of the character of the ore under treatment to insure complete decomposition. The boiling is continued until the fumes of sulfuric acid appear distinctly.

The casserole is then removed from the hot plate, contents allowed to cool and the sulfuric acid solution diluted with water to three or four times its bulk, and chlorate of potassium added whether manganese be present or not.

If manganese is present the chlorate must be added in quantity sufficient to insure complete precipitation, an additional quantity of this reagent being added during the boiling if it appears necessary.. This can be easily determined by the appearance of the solution. The precipitated manganese dioxid and the insoluble residue are now filtered off and well washed with boiling water.

To the filtrate ammonia water is added *in slight excess*, the precipitate well stirred and immediately filtered off, the filtrate passing into a graduated flask of 250 cc. capacity.

After the iron and alumina precipitate has been transferred to the filter—which should be a sufficiently capacious one—it is allowed to drain thoroughly, and then washed three or four times with water which has been rendered distinctly ammoniacal, and which should not be more than *tolerably* warm. In washing the precipitate care should be taken to thoroughly disintegrate it by the stream of wash water.

After a thorough washing the filtrate is acidfied by hydrochloric acid, the flask filled to the mark, its contents well mixed, and a number of aliquot portions of the solution taken from the zinc determination, which is accomplished by a standardized solution of ferrocyanid of potassium, acetate of uranium being used as indicator.

If copper is present it must be removed previous to titration by means of granulated lead. The titration is always made in hot solutions.

Results were as follows:

No. 5	[illegible] per cent. zinc
" 9	[illegible]
" 11	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Notes on the above method:

Attention has been called to the advisability of washing the iron precipitate with water which is not more than tolerably warm, it having been the writer's experience that a partial precipitation of the hydrated oxid of zinc takes place more easily from solutions which, while yet distinctly ammoniacal approach more nearly the boiling temperature. The precipitation of the hydrated zinc oxid is furthermore influenced by the precipitation of the hydrated sesquioxid of iron, especially so when the solutions are very hot.

To prevent this occurence the precautions previously indicated must be observed, in addition to which as a further safe guard wash water, which has been rendered ammoniacal, or has been impregnated with chlorid of ammonium is used.

Method of Mr. F. Mentzel, Superintendent of San Juan Smelting and Mining Company, Durango, Colorado.—The method about to be described is based on the principle that in an almost neutral solution of sulfates or chlorids, the separation of zinc from iron, manganese, cobalt, and nickel can practically be effected by means of hydrogen sulfid, while if the solution contains about one tenth of its volume of sulfuric acid the separation of zinc from copper is equally complete provided the solution is heated almost to the boiling point before the precipitated sulfids are filtered off.

The *modus operandi* is as follows:

One gram of ore is decomposed in an eight ounce flask with five cc. conc. hydrochloric and five cc. conc. nitric acid; after the red fumes have ceased to be evolved, five cc. conc. sulfuric acid are added and the whole evaporated until the fumes of sulfuric acid appear. It is absolutely essential at this point that all traces of nitric acid shall have been expelled as otherwise erroneous results will be obtained.

On the appearance of the sulfuric acid fumes the flask is

moved from the hot plate, allowed to cool, about fifty cc. water added and a brisk current of hydrogen sulfid passed through the solution. In a few minutes the precipitation of the copper, etc., will have taken place. The precipitation is complete when the precipitated sulfids are seen to settle rapidly at the bottom of the flask.

Now heat the solution as rapidly as possible almost to the boiling point, by which most of the absorbed sulfuretted acid will be expelled; any zinc which may have been precipitated will by this means be redissolved. Filter into a sixteen ounce flask, wash the precipitate with cold water three or four times, allowing the filter to run dry each time before renewing the wash water.

After washing neutralize the filtrate with ammonia water, care being taken not to let the ammonia run down the sides of the flask, but to drop it directly into the liquid, the solution being constantly agitated while being neutralized. It is advisable to add a slight excess of ammonia, the ferrous hydrate precipitate being again redissolved by a few drops of dilute sulfuric acid (1 : 4). A slight permanent turbidity is of no consequence.

Now add an excess of four to six drops of dilute sulfuric acid, fill up the flask with water, and again introduce a brisk current of hydrogen sulfid into the solution. Within five to ten minutes a heavy sandy or powdery precipitate of whitish or yellowish zinc sulfid will appear, the rapid settling of which, and the clear supernatant liquid being an indication of complete precipitation. The precipitate filters rapidly and is indifferent to the influence of air, either during filtering or washing. It is filtered off and thoroughly washed, about five washings being usually sufficient unless the solution contained much iron.

The zinc sulfid which has adhered to the flask and the glass tube is now dissolved in three to five cc. of hydrochloric acid, the solution diluted with an equal amount of water and then poured on the filter containing the precipitate, which should immediately thereafter be covered with a watch-glass. The greater part of the precipitate dissolves easily, the solution of any undissolved portion being effected with a few drops of conc. hydrochloric acid.

The bulk of free acid in the solution is now neutralized with ammonia water, and the zinc determined by titrating with standardized solution of ferrocyanid of potassium, using acetate of uranium as an indicator.

The following are the results obtained:

	Per Cent Zinc			
	No. 9	No. 11	No. 13	No. [illegible]
	21.61	11.17	[illegible]	[illegible]
	21.[illegible]	11.11	[illegible]	[illegible]
	21.[illegible]	10.[illegible]	[illegible]	[illegible]
	21.[illegible]	10.[illegible]	[illegible]	[illegible]
Average	21.[illegible]	11.[illegible]	[illegible]	[illegible]

Method of Dr. H. C. Hahn, Chemist Colorado Smelting Company, Pueblo, Colorado.—The following method is one in which the determination of manganese as well as zinc is effected in the same solution.

Five-tenths of a gram of ore is treated in a porcelain casserole with two cc. conc. nitric, three cc. dilute sulfuric (1 : 2), and six cc. conc. hydrochloric acids, evaporated to dryness, or until the fumes of sulfuric acid appear. The casserole is then removed from the hot plate and allowed to cool, when twenty cc. water are added and the solution heated to boiling for about one minute.

The contents of the casserole are now transferred to an eight ounce beaker, and the solution nearly neutralized with a saturated solution of carbonate of sodium. In case too much of the latter should have been used, acidify with a few drops of dilute sulfuric acid.

Now add to the solution an excess of basic carbonate of lead suspended in water until after vigorous stirring the precipitated hydroxid of iron settles quickly to the bottom of the beaker, leaving the liquid clear.

The solution should measure now about eighty cc. It is heated to boiling without previous filtration, and the manganese determined with a standardized solution of permanganate of potassium (4.80 grams of potassium permanganate to a liter, whereof one cc. equals 0.50 per cent. Mn).

After each addition of the permanganate the solution should be briskly stirred, as it facilitates the settling of the precipitate. Should the solution appear yellow or turbid, the stirring must be

continued until it is clear. When the rose tint appears, indicating the complete precipitation of the manganese, a few grams of chlorid of ammonium and five cc. ammonia water are added, and the solution is filtered without previous heating, the precipitate being washed with water containing about one-fifteenth of its bulk of strong ammonia water.

The precipitate is well washed, and to the filtrate, which should measure about 140 cc., 12½ cc. of hydrochloric acid are added. If copper is present it is removed by means of granulated lead, after which the zinc is determined by titrating with a standardized solution of ferrocyanid of potassium, an uranium salt being used as indicator.

The manganese determination is quite exact, but the zinc determination not so good.

The results on samples of ore submitted are:

	Per Cent. Zinc.				
	No. 5.	No. 9.	No. 11.	No. 13.	No. 20.
	14.38	22.95	8.58	5.24	13.40
	14.22	23.11	9.20	5.64	12.84
Average,	14.30	23.03	8.89	5.44	13.22

	Per Cent. Manganese.				
	No. 5.	No. 9.	No. 11.	No. 13.	No. 20.
	3.22	2.89	2.68	9.25	0.65
	3.32	2.81	2.72	9.53	0.87
Average,	3.27	2.85	2.70	9.39	0.76

Note:

The basic carbonate of lead used in the preceding method is prepared by adding to a hot solution of carbonate of sodium, a hot solution of acetate of lead as long as a precipitate is formed and washing the precipitate repeatedly by decantation until all sodium salts are removed.

COMPARISON OF RESULTS.

Analyst.	No. 5.	No. 9.	No. 11.	No. 13.	No. 20.
Eakins	14.64	24.11	10.71	6.31	16.09
Von Schulz & Low	15.31	24.34	10.76	6.42	16.14
Jones	15.39	24.53	10.83	6.58	16.46
Hawkins	15.66	24.23	11.88	8.73	15.86
Knight	15.08	23.80	10.69	6.85	15.90
Page	14.62	22.00	10.50	6.30	15.37
Mentzel	——	23.62	11.07	6.89	16.08
Hahn	14.30	23.03	8.89	5.44	13.22

A consideration of the above results leads to the conclusion that there are a number of the methods detailed that are satis-

factorily adapted for the technical determination of zinc. All of the technical chemists employ the ferrocyanid solution for the final titration.

A method, however, like the one used by Mr. Mentzel would hardly commend itself on account of the repeated use of hydrogen sulfid. The unique method of Dr. Hahn for the combined determination of manganese and zinc from one solution is open to the serious objection that the zinc results are uniformly low. With this difficulty obviated, the method would be a highly commendable one.

The governing factors which should influence the selection of any given method for general adoption in technical laboratories are without doubt the accuracy of the results that can be obtained by its use, together with the time involved in its execution. When it is borne in mind that the technical chemist is fairly confronted with a large number of determinations that are to be made, and that not only are metallurgical calculations but also treatment charges on ores dependent on his results, the desirability of having simple, quick, and correct analytical methods is made apparent.

Without at all disparaging the methods employed by Messrs. Page, Hawkins, and Knight, it seems to the committee that the method described by Messrs. von Schulz & Low approximates more nearly the conditions prescribed than do any of the others. It will be noted that the results given by Messrs. von Schulz & Low are comparatively high only in their determination of samples Nos. [illegible] and attention is directed to the fact that in both of these samples the presence of cadmium is noted. Mr. Hawkins's sample No. [illegible] containing the larger quantity. It is to be regretted that Mr. Hawkins did not furnish the exact amount of cadmium contained, but his results on this element were not reported by the committee at the time the [illegible] submitted to them for analysis.

The committee believe that the ores on which the various gentlemen were made were such as have selected the methods [illegible]

in the determination of zinc to a severe test. It is also aware that any method which would commend itself for general introduction must not only be a satisfactory one in the hands of its originators, but that it must also be capable of yielding concordant results when operated by others. This can only be determined by a fair and impartial trial.

If the inducements pertaining to von Schulz and Low's zinc method seem sufficient to warrant other chemists in investigating its merits, the committee will be glad to aid such in furnishing requisite material; and it will no less be pleased to publish such criticism as may be offered, if weaknesses in the method which are not now apparent, are thereby disclosed.

NOTE BY THE EDITOR.—The following corrections from von Schulz and Low were received too late for insertion in the proper place: "After the word 'solution', thirteenth line from top of page 492 add the following: Owing to the fact that ores rich in sulfur occasionally react too violently by this treatment it is best to vary the method in such cases by first adding five cc. strong nitric acid to the ore and heating in a covered casserole until the mass begins to become pasty, and then remove from the heat and add twenty cc. of the chlorate solution and finish the evaporation as usual.

"'Uranium acetate,' p. 491, fourteenth line from bottom, and p. 493, the ninth and the fifteenth line from bottom should read 'uranium nitrate.'"

THE QUALITATIVE DETECTION OF NICKEL AND COBALT.*

BY FRED. J. HAMBLY.

The qualitative detection of nickel in presence of cobalt is often a difficulty with the beginner in the study of analysis. When the conditions are correctly understood, Liebig's cyanid separation,—the essential details of which were fully worked out by Gauhe (*Ztschr. anal. Chem.*, 1866, p. 75) in 1866,—is, in the writer's experience, the simplest and most rapidly executed. Although clearly stated by Fresenius in his *Qnantitative Analysis*,† so far as I am aware, there is not one of all the multitude of text-books on qualitative analysis in our language which recommend this method that does not introduce some unnecessary condition into the procedure, as in most cases the student's difficulties arise not from his own incapacity, but from the faulty description given by his text-book.

*Chem. News, 65, 289.

† Seventh English Edition, 1, 444. In his *Qualitative Analysis* Fresenius adopts the more tedious nitrite separation.

Although the subject is not original, it may therefore be useful to call the attention to the simplest and most satisfactory method of working. Gauhe shows conclusively that the conversion of potassium cobaltous cyanid into the cobalticyanid by boiling with hydrocyanic acid (at best a dangerous experiment), is always incomplete; but that by means of a suitable oxidizing agent in alkaline solution the cobalt may be directly converted into the soluble cobalticyanid, the nickel being simultaneously precipitated as hydrated nickelic oxid. The method of detecting nickel in presence of cobalt is then as follows: Separate the mixed sulfids from the ammonium sulfid precipitate by means of cold dilute hydrochloric acid, and test a small portion in a borax bead. The presence or absence of anything more than a trace of cobalt is directly indicated by the coloration produced. Dissolve the sulfids in hot hydrochloric acid with the aid of potassium chlorid, boil off the excess of chlorin and remove the excess of acid either by neutralization or evaporation to dryness. To the neutral solution add an excess of freshly prepared solution of potassium cyanid in cold water, *beyond* what is necessary to redissolve the precipitated cyanids. Boiling is unnecessary. Make the solution decidedly alkaline with sodium hydrate, add about twice the volume of bromin water, heat gently, allow to stand a few minutes, and filter off the precipitated nickelic oxid. The nickel may be confirmed by the borax bead reaction after washing the precipitate.

The action of the oxidizing agent can be represented by equations, thus:

$$2KCNCo(CN)_2 + 2KCN + Br = K_6Co(CN)_6 + KBr$$

$$2KCNNi(CN)_2 + 3NaOH + Br = Ni(OH)_3 + NaBr + 2KCN + 2NaCN$$

There is no liberation of hydrocyanic acid at any stage of the process, so the operations may be safely conducted in the open laboratory. Commercial cobalt salts almost invariably give a precipitate of nickelic oxid. The cyanid method has the advantage over the precipitation of the cobalt as potassium cobaltinitrite in that the separation is most frequently carried out with the object of detecting nickel, which metal is immediately separated as a precipitate readily available for examination.

If the analysis is to include a search for traces of cobalt, the alkaline filtrate from the nickel precipitate is, *in the draught cupboard*, acidified with excess of sulfuric acid, and evaporated until the excess of acid is nearly expelled. The residue is taken up with water, made alkaline with ammonia, the cobalt, if present, precipitated by ammonium sulfid, and confirmed by the borax bead. Or, a portion of neutral solution, containing the nickel, may be treated with acetic acid and potassium nitrite, and the traces of cobalt directly precipitated by allowing to stand for a few hours.

NOTE ON THE EFFECT OF SEDIMENTATION ON THE SELF-PURIFICATION OF RUNNING STREAMS.*

[CONTRIBUTIONS FROM THE LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE.]
BY W. P. MASON AND C. C. AROSEMENA.

The question of sedimentation is one which has been considered by some authorities as of vital importance in the self-purification of streams. With a view of determining to what extent it can be depended upon, the following investigation was undertaken.

Upon four different occasions (covering various conditions of medium, high water, and flood) samples were analyzed from that section of the Hudson River extending between Troy and Albany. The stations at which samples were taken were situated a little over one mile apart, beginning at State street, Troy, and ending at the Albany Intake, five miles below. Two samples were taken at each station during ebb tide and in mid-channel; one two feet from the surface and the other, as near as could be judged, two feet from the bottom.

The bottom samples are designated throughout this paper by priming the letter used to designate the corresponding upper sample. The letters used are from A to F inclusive.

The first set of samples was taken on April 26, the river being two feet above normal. The appearance of the water at that

*The following was presented by Mr. Arosemena as a graduation thesis for the degree of B. S., at the Rensselaer Polytechnic Institute, in June, 1892. The work is entirely his own, and was undertaken at my suggestion and under my observation.
W. P. Mason.

time was clear, and, owing to warm weather during the early part of April, all snow water was probably absent from the river.

The second set of samples was taken on May 12, the water being 4.2 feet above normal. The state canals had already been opened and numerous tugs and steamboats agitated the water. It had rained on the previous day. The water appeared clear.

The third set of samples was taken on May 23, the water being very turbid and reading 11.5 feet above normal.

On May 31 the fourth and last set of samples was collected. The water was still high, reading 9.5 feet above normal and was very turbid.

All samples were analyzed as soon as obtained and the analytical results expressed, in parts per million, as well as their graphical representation, are given beyond (the charts are omitted). From the examination of these data, the conclusion seems to be justified that water containing a considerable amount of suspended matter capable of settling is to a certain degree purified, in accordance with the well known laboratory observation that solid material, no matter how minute, on settling will often drag with it and precipitate more or less other materials even though the latter be in solution.

As expected, total solids were higher during flood; at the same time the analysis showed the water in a poorer condition than when the river was low, even though the dilution was much greater. This is to be accounted for by the fact that during high water a great increase of surface washing occurs which also carries greatly increased impurities to the main stream.

The examination of the total solids shows sedimentation at all stages of the river, the average being nearly constant throughout the entire distance.

Such sedimentation is, however, decidedly small. An idea of the amount deposited may be obtained from the [illegible] average differences between the upper and the lower sampling stations. At station C is 3.47 per cent of the total solids in the upper sample. A glance at the table of required oxygen can not do [illegible] than disclose the fact that sedimentation has taken place; [illegible] in this case the percentage of improvement is much smaller than what is indicated by the total solids. The fact that there [illegible]

has increased shows that a step toward oxidation has taken place.

During flood, albuminoid ammonia has increased, owing to more fresh organic matter coming into the stream and decomposing from the first to the second stage of oxidation.

In order to get some idea of general purification, the following is a tabulated statement showing the amount of each ingredient in the upper sample at Albany as compared with the corresponding one at Troy. The calculations are based on the average results in parts per million.

	Troy.	Albany.
Free ammonia	0.0418	0.6000
Albuminoid ammonia	0.1667	0.1550
Required oxygen	6.5310	5.8750
Nitrates	0.4636	0.4872
Total solids	94.2500	116.0000

Nitrites were found in traces only. The results on required oxygen show some improvement, but the differences are too small to be noteworthy. Nitrates have a tendency to run high in lower samples, giving signs of oxidation, but such oxidation appears to be exceedingly slow, judging from the results here obtained.

A review of the evidence herewith given leads to the belief that sedimentation is at times a source of river purification in streams such as the Hudson, although not nearly so pronounced a one as has been heretofore held.

FREE AMMONIA.

	1	2	3	4	Average.
A	0.0425	0.0350	0.0375	0.0550	0.04187
A′	0.0325	0.0250	0.0175	0.0550	0.03250
B	0.0650	0.0260	0.0175	0.0800	0.04172
B′	0.0750	0.0260	0.0200	0.0500	0.04275
C	0.0600	0.0550	0.0900	0.0550	0.06500
C′	0.0700	0.0450	0.0400	0.0400	0.04875
D	0.0413	0.0600	0.0550	0.0650	0.05542
D′	0.0400	0.0350	0.0550	0.0700	0.05000
E	0.0375	0.0450	0.0550	0.0600	0.04947
E′	0.0375	0.0350	0.0540	0.0400	0.04287
F	0.0200	0.0600	0.0820	0.0800	0.06000
F′	0.0200	0.0500	0.0610	0.0650	0.04900

ALBUMINOID AMMONIA.

	1	2	3	4	Average
A	0.1375	0.1700	0.1925	0.1670	[illegible]
A'	0.0975	0.1200	0.1995	0.1550	[illegible]
B	0.1550	0.1900	0.2225	0.1000	[illegible]
B'	0.1750	0.1800	0.2150	0.1250	[illegible]
C	0.0950	0.0850	0.2450	0.1700	[illegible]
C'	0.1050	0.1100	0.2750	0.1350	[illegible]
D	0.0837	0.0900	0.2400	0.1750	[illegible]
D'	0.1300	0.1200	0.2500	0.1350	[illegible]
E	0.1105	0.1350	0.2100	0.1900	[illegible]
E'	0.1275	0.1200	0.1950	0.1700	[illegible]
F	0.1200	0.1150	0.2000	0.1850	[illegible]
F'	0.0950	0.1300	0.2050	0.1350	[illegible]

NITRATES.

	1	2	3	4	Average
A	0.5125	0.4992	0.4996	0.3432	[illegible]
A'	0.6314	0.5000	0.4246	0.3432	[illegible]
B	0.6028	0.5047	0.4246	0.3696	[illegible]
B'	0.7400	0.5879	0.4224	0.3960	[illegible]
C	0.4830	0.4796	0.4488	0.3916	[illegible]
C'	0.5984	0.5072	0.6688	0.4048	[illegible]
D	0.4960	0.4752	0.4796	0.3828	[illegible]
D'	0.4972	0.4092	0.4796	0.3784	[illegible]
E	0.4994	0.4004	0.4796	0.4752	[illegible]
E'	0.4994	0.4092	0.5085	0.4884	[illegible]
F	0.4928	0.5032	0.5056	0.3872	[illegible]
F'	0.4928	0.5720	0.5023	0.4136	[illegible]

REQUIRED OXYGEN

	1	2	3	4	Average
A	5.6500	5.8500	7.8750	6.7500	[illegible]
A'	5.7000	5.6500	7.8750	6.7500	[illegible]
B	5.8000	6.7500	7.1000	7.1500	[illegible]
B'	5.6000	6.7500	6.6000	7.3500	[illegible]
C	4.8500	4.3500	6.9500	5.7000	[illegible]
C'	5.5000	5.6000	7.5000	5.5500	[illegible]
D	5.2000	4.9500	6.8000	5.2500	[illegible]
D'	5.3500	4.6000	7.3500	6.8000	[illegible]
E	5.1000	6.3000	7.1000	6.2000	[illegible]
E'	5.3500	6.7000	7.6000	6.2000	[illegible]
F	4.9500	5.7000	7.5000	5.8000	[illegible]
F'	5.3500	5.4000	7.3500	5.7500	[illegible]

TOTAL SOLIDS.

	1	2	3	4	Average.
A	63.00	60.00	150.00	90.00	94.25
A′	48.00	62.00	151.00	99.00	90.00
B	54.00	55.00	149.00	98.00	89.00
B′	55.00	57.00	149.00	100.00	90.25
C	63.00	64.00	153.00	101.00	95.25
C′	63.00	64.00	163.00	104.00	98.50
D	65.00	86.00	165.00	96.00	103.00
D′	66.00	89.00	169.00	99.00	105.75
E	73.00	56.00	166.00	92.00	96.75
E′	78.00	59.00	170.00	90.00	99.25
F	80.00	90.00	179.00	115.00	116.00
F′	82.00	91.00	172.00	110.00	113.75

ANALYSIS OF LIME ROCKS FROM MAINE.

By Franklin C. Robinson.

The chief lime region of Maine is in Knox and Lincoln counties in the towns of Rockland, Thomaston, and Warren. Lime has been burned in that locality for a century or more and its reputation for building purposes is of the highest. I have recently had samples of the rock, which I collected myself, analyzed in my laboratory, and they show the general character which such lime must have.

The rock shows little sign of crystallization, but is gray, massive or finely granular, with appearance of stratification. Two kinds of rock are distinguished by the miners, called "soft rock" and "hard rock." The hard rock evidently contains more silica, and when it contains so much as to injure the quality of the lime it is called "poor rock." Streaks of poor rock are found in all the quarries and many have been abandoned on that account.

It will be noticed that the magnesia is small in most of the Rockland limes, but still it is always present and in one case amounts to over twenty per cent. On the other hand, some of the Warren rocks are true dolomites. These latter, too, are whiter in color, and show distinct crystallization and cleavage.

Local names of quarries are given, but all those analyzed in

each town are in close proximity, except that from Case and Glover vein, which is a mile or more from the others in Rockland.

	Soft rock, Engine Quarry.	Soft rock, Doherty Vein.	Hard rock, Doherty Vein.	Hard rock, Engine Quarry.	Soft rock, Ulmer Drain Quarry.	Soft rock Case & Glover Vein	Dolomite from Warren.	Dolomite from Warren.
Silica	0.87	1.8	2.52	2.48	0.90	1.3	5.8	4.50
Iron and alumina	0.12	0.3	0.63	0.22	0.01	0.6	0.2	0.36
Calcium carbonate	98.60	77.2	93.85	95.94	98.90	98.6	52.2	53.72
Magnesium carbonate	0.22	20.8	2.79	1.27	0.41	trace	42.0	41.33
Total	99.81	100.1	99.79	99.91	100.22	100.5	100.02	99.91

Much credit is due Mr. C. H. Cutts for the careful manner in which the analyses were made.

CHEMICAL LABORATORY OF BOWDOIN COLLEGE.

PHOSPHORIC ACID IN BERYL.

BY FRANKLIN C. ROBINSON.

Several years ago (Spring of 1883) Prof. J. Torrey, Jr., now of the Harvard Laboratory, then a student in Bowdoin, found a mineral in the neighboring town of Yarmouth which was of such peculiar appearance that I suggested that an analysis be made. Its appearance suggested a beryl; that is, it was of the well known beryl form, but had hardly the suggestion of green color and the crystallization was rather indistinct. His analysis gave silica lower and alumina higher than they should be in beryl, and in addition phosphoric acid and alkalis were discovered to the amount of several per cent. Our notes, made at the time, show that while sodium and potassium were the chief alkalis in amount, undoubted traces of lithium and caesium were also present.

Our decision then was that the mineral was probably not a beryl, and it was laid aside for future work. Since then, as is well known, other observers have proved the general presence of alkalis in beryl, and I have only awaited a favorable opportunity to re-examine the specimen and see if, after all, our first

impression as to its being a beryl may not have been correct. My assistant, Mr. C. H. Cutts, has now made such re-examination with the following results:

Color, gray to white, with mere trace of green. Hardness, 7. Specific gravity. 2.627. Loss on drying at 100° C., 0.33 per cent.

	PER CENT.
Loss on ignition	1.53
Silica	64.70
Alumina	17.76
Beryllium oxid	12.18
Phosphoric acid	2.76
Alkalis (Na_2O, K_2O, Li_2O, Cs_2O)	1.10
	100.03

Regarding the phosphoric acid and alkalis as replacing a part of the beryllium, we have the numbers 1, 2, 6, 12, for water, alumina, beryllium oxid, silica, respectively, showing that the mineral is really a beryl. The former low result in silica was not obtained owing to greater care in selecting a pure specimen for analysis.

The presence of phosphoric acid in this led me to have it tested for in other specimens of beryl, with the result that its presence has been detected in nearly every case; but in no other specimen has so large a percentage been found. I am unaware that any notice of the fact that phosphoric acid is frequently present in beryls has before been published.

CHEMICAL LABORATORY OF BOWDOIN COLLEGE.

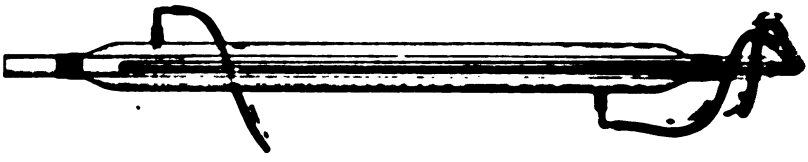
AN EFFECTIVE CONDENSER FOR VOLATILE LIQUIDS AND FOR WATER ANALYSIS.

BY W. A. NOYES.

An effective condenser has recently been described by Evers.* The condenser illustrated by the cut below is similar in principle but has the advantage that it can be easily made from ordinary laboratory materials. A small glass tube is selected about twice as long as the internal tube of a Liebig's condenser, and having an external diameter a little less than one-half as great as the internal diameter of the tube of the condenser. The tube is bent sharply on itself in the middle, taking care to bring the two sides close enough together at the bend so that the

* *Ber. d. chem. Ges.*, 24, 3950.

U tube formed will enter the internal tube of the condenser. The tube must not, however, close upon itself at the bend in such a way as to impede the flow of water through it. The two ends of the tube are bent over so as to form an angle of about forty-five degrees. The small tube is then inserted into the lower end of the Liebig's condenser with the bent ends directed



upward. The tube and condenser are connected with the water supply in such a way that the water passes first through the small tube and then through the outer tube of the condenser.

I have found the condenser especially useful in water analysis in determining ammonia, where it is essential that the distillate should be thoroughly cooled. I am indebted to Mr. A. V. H. Mory for the accompanying drawing.

Rose Polytechnic Institute, Oct. 1893.

THE DETECTION AND ESTIMATION OF MINUTE QUANTITIES OF LEAD IN THE PRESENCE OF COPPER AND IRON.*

By Frank F. Tredick.

I propose first to refer to the detection of lead in sulfuric acid. The usual method is by dilution with water, but I found [illegible] years ago, that by adding hydrochloric acid to the sulfuric acid and keeping it cold, a much smaller quantity of lead could be detected than by adding water, or even by adding water and subsequently an equal volume of absolute alcohol. The lead is precipitated as chloride as a peculiar pearly opalescence. I patented this process for the purpose of removing lead from sulfuric acid, which it does perfectly, but sulfuric acid manufacturers assure me that there is no commercial value in any process that would effect such a result. Although leaving something [illegible]

* [illegible]

desired as a patent, the process is still of use as a test on account of its delicacy. It can be applied to the detection of minute quantities of lead in organic substances. Take, for instance, a substance which is generally, I may say invariably, contaminated with lead—tartaric acid. The lead is a little difficult of detection by the ordinary process, because sulfid of lead, as we know, is more or less soluble in tartaric acid. If the tartaric acid is ignited, a large proportion of the lead is, of course, lost, but some is left, and there is sufficient in the small quantity of ash, if digested with pure sulfuric acid, to show the characteristic reaction on the subsequent addition of hydrochloric acid. While on the use of hydrochloric acid as a test for lead in sulfuric acid, I may mention that nitric acid is also a test for lead in sulfuric acid; but it is not nearly so delicate as hydrochloric acid. If to a sample of commercial sulfuric acid which is very rich (*i. e.*, very impure) in lead, nitric acid is added, the lead mainly settles out, but still, after treatment with nitric acid, lead can be detected by the addition of hydrochloric acid. Hydrochloric acid gas is insoluble in sulfuric acid, and if passed through strong sulfuric acid which is highly contaminated with lead for an hour or more, nothing whatever happens; but if to that acid in a test tube a single drop of the solution of hydrochloric acid, or a crystal of common salt is added, the characteristic precipitate at once appears.

The main object of my paper was to draw attention to the difficulty of detecting and estimating minute quantities of lead in presence of copper and iron. There are certain temperance drinks, such as lemonade and soda water, which, in the process of manufacture, are liable to contain at least these three metallic impurities. In the case of lemonade, the lead occurs partly in the tartaric acid used, and partly comes from the use, perhaps one ought to say abuse, of lead pipes for transferring the charged solutions; and the copper comes from the copper cylinders (although tin-lined) in which the drink is charged with carbonic acid. Hence the difficulty arises of detecting a highly poisonous metal like lead, in the presence of a mildly poisonous metal like copper, and a non-poisonous metal like iron. The most delicate reaction for both lead and copper is, I believe, the

precipitation as sulfids, either by hydrogen sulfid or ammonium sulfid. The amounts present can, of course, be estimated colorimetrically by comparison with known quantities. I find the sulfid reaction far more delicate in the case of copper than the ferrocyanid reaction. I do not think the hundredth of a gram of copper in a gallon of liquid could be detected by means of the ferrocyanid reaction without concentration, but ammonium sulfid would easily detect it. The objection to this reagent is that it does not distinguish between lead and copper. To effect this distinction I simply make use of the well-known fact that sulfid of copper is soluble in cyanid of potassium, whereas sulfid of lead is not. To perform a determination: Place a measured quantity of lemonade, or other liquid, in a cylinder or white basin. Add a few cc. of ammonia and a little cyanid of potassium, then add a minute quantity of ammonium sulfid. Down comes the lead, but not the copper. Then imitate the color by known quantities of lead precipitated under similar conditions. Iron does not at all interfere with the test. If an iron salt is added to lemonade, for instance, and made alkaline with ammonia, the iron is kept in solution by the tartaric acid and on addition of cyanid of potassium is converted into a ferro- or ferricyanid, not precipitable by ammonium sulfid. In the case of liquids not containing tartaric acid, it is easy enough to add a little in the event of iron being present.

DISCUSSION.

Mr. Bertram Blount said that with reference to the general question of testing for lead in small quantities, that there was one test, the merits of which Mr. Allen and Mr. Harvey had done much to make known. He referred to the chromate test, which he constantly used for all purposes; it was not only exceedingly delicate if properly carried out, but also extremely characteristic.

Mr. Sidney Harvey said that in water containing a [illegible] part of a gram of lead per gallon the metal could be precipitated by bichromate of potash. If allowed to stand for [illegible] hours the water could be poured off to the last drop, and the chromate of lead could then be advantageously stirred up with a little distilled water and turned into a smaller vessel, say a [illegible]

inch test tube, when a precipitate visible both by color and amount would quickly settle.

Mr. E. Russell Budden said he had found that when the chromate test was used in the presence of organic matter, a reduction always took place. For instance, in a case of testing for lead in lemonade, if one used the chromate test with the original liquid, and allowed it to stand for a time, in a great many cases, presumably from the fact of tartaric acid or other reducing agents being present, a green chromium salt was produced, and the chromate precipitate was practically unobservable. He did not know whether any of the members had observed the same thing, but it had been an insuperable difficulty with him in applying the test in presence of organic matter. Whilst speaking of the chromate test, he would mention that he had adopted the method of observing it under different conditions of light to those usually recommended. He believed the usual method was to place the water in a cylinder or vessel of some kind to allow of settlement and decantation. He had found that if the test were observed in an ordinary light, very frequently a *minute* trace of lead escaped observation; but if the light were shed in such a way that an oblique beam fell through the liquid, all other light being excluded, a characteristic opalescence could be detected. He used a square box sufficiently large to contain a good sized flask, and so constructed that the light came only through an aperture in the upper part. By adopting this method, he was able to detect exceedingly minute quantities of lead in waters, quantities which, without these precautions, the method utterly failed to give any indication of. He had been worrying over this matter for a very long time, and had tried the experiment in presence of copper and other metals. In addition to the two or three metals mentioned by Dr. Teed, tin was occasionally present in artificial mineral waters; and he had also found traces of antimony. He believed the President could bear him out so far as the tin was concerned.

Dr. Teed, in reply, said that he was obliged, in testing lemonades, to abandon the chromate test for reasons similar to those mentioned by Mr. Budden. He would like to know whether Mr. Blount or any other member had personal experience with

the chromate test in presence of tartaric acid or other organic matters, such as occurred in commercial lemonades. With regard to the presence of tin and antimony, they would not interfere with the test for lead, it being performed in an alkaline solution with ammonium sulfid as the precipitant.

THE SEPARATION OF LIME AND MAGNESIA FROM ZINC AS PHOSPHATES

By George C. Stone

Wishing to find a method of separating lime and magnesia from zinc that did not necessitate the use of the very troublesome sulfid of zinc, it occurred to me that, as phosphate of zinc was very soluble in ammonia and phosphates of lime and magnesia were insoluble, possibly a method could be based on this reaction. My first experiments, with very small quantities of lime and magnesia, were satisfactory; but later, when I tried to separate zinc from larger quantities, the results were low. Knowing that the presence of ammonium chlorid increases the solubility of zinc salts I next tried adding some to the solution with more satisfactory results. It appeared probable that manganese could be separated from zinc by the same reaction, but this proved not to be the case, because it is necessary to heat the precipitate of phosphate of manganese until it crystallizes in order to completely precipitate the manganese, and if the solution is heated some zinc precipitates.

After making a number of experiments to find the proper amounts of ammonia and ammonium chlorid to use I finally adopted the following method which has been uniformly successful.

Ammonia Solution.—Make a solution of two gms. ammonium chlorid in 700 cc. of strong ammonia and dilute to one liter.

Nearly neutralize the cold solution containing lime, magnesia and zinc with ammonia and add fifty cc. ammonia solution and one cc. of a ten per cent. solution of salt of phosphorus for each gm. of zinc present. A larger excess does no harm. Allow the precipitate to settle, filter and wash three times with [illegible] per cent. ammonia. Dissolve in hydrochloric acid, add a little salt

of phosphorus, precipitate by twenty-five cc. ammonia solution, let settle, filter and wash as before. Combine the filtrates and washings, nearly neutralize with nitric or sulfuric acid, and make slightly acid with acetic acid,* heat to about 80° C. until the precipitate crystallizes, filter and wash well with hot water, dry, ignite, cool, and weigh as $Zn_2P_2O_7$.

If mere traces of lime and magnesia are present one precipitation is sufficient; but if more than three or four milligrams are present two should be made. The amount of ammonia solution used should be in proportion to the lime and magnesia present. With small amounts rather less than the quantities given above will answer, but with larger quantities it is better to use more than twenty-five cc. for the second precipitation.

Separation of Zinc from Lime.—I made solutions containing the amounts of lime and zinc given below. For Nos. 1 and 2 I used twenty-five cc. ammonia solution for each precipitation; for Nos. 3 and 4, fifty cc. for the first and twenty-five cc. for the second; and for Nos. 5 and 6, fifty cc. for the first and thirty cc. for the second.

No.	Gms. Lime Taken.	Gms. Zinc Taken.	Gms. Zinc Found.	Error.
1	0.112	0.4644	0.4633	—0.0011
2	0.112	0.2322	0.2317	—0.0005
3	0.224	0.2322	0.2339	+0.0017
4	0.224	0.1161	0.1150	—0.0011
5	0.448	0.1161	0.1140	—0.0021
6	0.448	0.0580	0.0566	—0.0014

The precipitate of phosphate of lime is very bulky and rather troublesome to wash, so that when very large it is apt to retain some zinc.

Separation of Zinc from Magnesia.—I tried a similar series with magnesia instead of lime. For all I used fifty cc. ammonia solution for the first precipitation; for Nos. 7, 8, 9, and 10 I used twenty-five cc., and for Nos. 11 and 12 I used thirty and thirty-five cc. for the second.

No.	Gms. Magnesia Taken.	Gms. Zinc Taken.	Gms. Zinc Found.	Error.
7	0.1138	0.4736	0.4725	—0.0011
8	0.1138	0.2368	0.2361	—0.0007
9	0.2275	0.2368	0.2360	—0.0008
10	0.2275	0.1184	0.1184	0.0000
11	0.4553	0.1184	0.1181	—0.0003
12	0.4553	0.0592	0.0585	—0.0007

* Large amounts of $NH_4C_2H_3O_2$ dissolve some $ZnNH_4PO_4$, but NH_4NO_3 and $(NH_4)_2SO_4$ do not. See this Journal, 5, 67.

The separation from magnesia is more complete and takes less time than the separation from lime.

Separation of Zinc from Lime and Magnesia.—The method used was the same but the amounts of ammonia solution varied considerably.

No.	Cc. Am. sol. for 1st ppn.	Cc. Am. sol. for 2nd ppn.	Gms. lime Taken	Gms. Mg Taken	Gms. Zn Taken	Gms. Zn Found	[illegible]
13	25	15	0.112	0.085	0.2122	[illegible]	[illegible]
14	25	15	0.112	0.085	0.2847	[illegible]	[illegible]
15	50	20	0.112	0.085	[illegible]	[illegible]	[illegible]
16	50	20	0.224	0.115	0.2122	[illegible]	[illegible]
17	50	25	0.224	0.115	0.2122	[illegible]	[illegible]
18	50	20	0.336	0.174	0.2122	[illegible]	[illegible]
19	50	25	0.336	0.174	0.2122	[illegible]	[illegible]

Increasing the amounts of ammonia solution gave better results in each case. Precipitates of lime and magnesia settle better and are more easily washed than lime alone.

The lime and magnesia can be separated by the method proposed by Chester* as follows: Dissolve the mixed phosphates in hydrochloric acid and nearly neutralize with ammonia [illegible] and while boiling add boiling oxalate of ammonia. Let settle, filter, and wash with hot water. Treat the oxalate of lime as usual. Cool the filtrate and precipitate the magnesia by ammonia. One precipitation of lime is sufficient. The two following separations were made by this method:

No.	Gms. lime Taken	Gms. lime Found	Gms. Mg Taken	Gms. Mg Found	Gms. Zn Taken	Gms. Zn Found
20	0.224	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
21	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

This method is not well adapted to separating very small amounts of zinc from large amounts of lime and magnesia. In such a case it would probably be best to precipitate the zinc as sulfid, decant off the clear solution through a filter, dissolve the precipitate, and separate as phosphates. Where the case is reversed, and there is a very small amount of lime or magnesia with much zinc, the phosphate method works well. Using a single precipitation with twenty-five cc. of ammonia solution gave:

No.	Gms. Taken	Gms. Taken	Gms. Found	[illegible]
[illegible] Lime	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] Magnesia	[illegible]	[illegible]	[illegible]	[illegible]

* Am. Chem. [illegible] p. [illegible].

CONCERNING THE CONSTANT TO BE USED IN CLERGET'S INVERSION PROCESS.

FROM THE LABORATORY OF BREYER AND SCHWEITZER, 159 FRONT ST., N. Y. CITY.]

The attempt made by Professor B. B. Ross in the August number of this journal to refute our criticisms of the action of the Official Agricultural Chemists, who changed the constant to be used for calculating the results of Clerget's process of inversion, only proves how well founded our objections were.

The arguments raised by Professor Ross in defense of the change as adopted by the Association of Official Agricultural Chemists are the following:

1. "The reporter, Dr. Stubbs, did not intend, so I understand, that the time of heating in inversion should remain at ten minutes as in the original Clerget method, but that the time employed should be fifteen minutes, as in the method published in the proceedings of 1889, and as in the elective method given in the proceedings of 1890, the omission of the correction as to time of heating being merely through inadvertence."

In answer to this we cite the directions given in *Bulletin No. 31*, page 233, for the execution of the modified Clerget method against which our criticisms were directed: "Place in hot water and heat quickly *to 68°C.*, keep this temperature for *exactly ten minutes;* remove, cool quickly to room temperature, and polarize, noting the temperature." From this peremptory direction it appears that Dr. Stubbs could not possibly have intended a heating for fifteen minutes at a temperature of 68° to 75° C., as Professor Ross wishes us to believe, but that he repeated the directions of the original Clerget method, which, for the better information of the reader, we quote from *Annales de Chimie et de Physique*, [3], **26**, 201:

"La liqueur déféquée, filtrée et rendue incolore, après avoir été soumise a une première observation, dont il est pris note, est introduite dans un matras, dont le col est marqué de deux traits de jauge indiquant l'un une capacité de 50 cubique centimètres et l'autre un volume de 55 cubique centimètres, de telle sorte que l'intervalle qui'existe entre les deux traits soit égal au dixième à de la capacité la plus grande. On verse la liqueur seulement

jusqu'à la hauteur du premier trait et l'on y ajoute jusqu'au niveau du second trait de l'acide chlorhydrique pur et fumant. On agite pour que le mélange soit complet et l'on place le matras dans un bain-marie après y avoir plongé un thermomètre. La température est portée au moyen d'une lampe à alcohol jusqu'à [illegible] en réglant la flamme de manière à ce que la durée de chauffage soit de dix minutes environ, on retire ensuite le matras du bain-marie et l'on dépose dans un second vase rempli d'eau froide.

We see that Clerget recommends a temperature of [illegible] C. for about ten minutes, as he was well aware of the fact that a higher temperature than 70° C. greatly affects the result of the determination, while heating for a minute more or less has no material influence on the result. The correctness of this observation has been verified by Landolt, Tollens, Herzfeld and their pupils. (Dammaueller, *Zeitschrift für die Rübenzuckerindustrie des deutschen Reiches*, 1888, p. 742).

Professor Ross' reference to the method given in the bulletins of 1880 and 1890 might lead the reader to infer that in the bulletin of 1891 only slight errors were contained which [illegible] easily be corrected by looking over the former publications. That such are not the facts will be seen by the following citations.

Bulletin No. 28, 1890, page 218. "Place in hot water bath and heat quickly to 68° C., keep at this temperature for exactly [illegible] minutes."

Bulletin No. 28, 1890, pages 218 and 224, elective method. "The flask heated for fifteen minutes at 67° to 70° C. in a water bath. *The temperature should not exceed 70° C.*"

Bulletin No. 21, 1890, page 147. "Contents are heated [illegible] water bath for fifteen minutes at a temperature of [illegible]."

The reader will see what a terrible confusion as to these points [illegible] varied amongst the Official Agricultural Chemists in September, 1889, the date of their meeting, when he notes that the [illegible] Official Agricultural Chemists adopted the above [illegible] spite of the fact that up to August, 1888, Landolt, Tollens, Herzfeld and their pupils had already published the results of researches concerning the influence of concentration and temperature upon the inversion liquid. It had been [illegible] stated by the above mentioned reliable authorities that a temperature

ture higher than 70° C. causes invert sugar to be decomposed and thus has a fatal effect on the result, while a small deviation from the time prescribed does not materially alter the final result.

The fact that such erroneous direction for the execution of the inversion could be given in September, 1889, is overwhelming proof of our charge of lack of knowledge of the chemical literature. The same charge applies to the authors of the report on methods of sugar analysis published by the Louisiana Sugar Chemists' Association. The report refers to experiments executed in the summer of 1889, as stated by B. B. Ross in *Bulletin No. 24*, page 179, and read before the Association of Official Agricultural Chemists in September, 1889. The experiments were superfluous because similar ones had been published at least one year before that time. Moreover, these experiments were faultily executed and the conclusions arrived at were necessarily erroneous. Nothing is said in those notes about the use of a temperature of 68° to 75° C.; on the contrary, we find there the repeated statement that the original Clerget method was employed, as shown by the following quotations:

Bulletin No. 24, page 180: (1) "Fifty cc. of this solution were next inverted in the manner prescribed by Clerget." (2) "A similar solution was inverted as previously described."

Therefore it is evident that in the experiments of the Louisiana Sugar Chemists' Association a temperature of 68° C. was employed, which as shown before, was the temperature originally used by Clerget, and Professor Ross is guilty of a misstatement by saying "this process is included in the methods of analysis given in the pamphlet referred to and provided that the sample after addition of the acid should be heated in a water-bath at 68° to 75° C. for a period of fifteen minutes."

However, Professor Ross tries to explain the low readings obtained by stating *now* that a temperature of 68° to 75° C. was employed for inverting the sugar solutions and cites as authority A. Wohl (*Ber. d. chem. Ges.*, 1890, **23**, 2084). Professor Ross entirely overlooks the fact that this publication of Wohl only incidentally refers to analytical processes and that it makes no pretence of directly bearing upon our subject. The readings obtained by Wohl were for solutions of high concentration

inverted by heating the same to 100° C. during one-half hour and longer with minimum amounts of acid. The conditions are so entirely different from those prevailing in the process used for analytical purposes, that it is really difficult to see how anybody can try to establish any connection between the two subjects. It seems that Professor Ross is not acquainted with the publication of Wohl* which does bear upon our subject and which refers to an investigation into the reliability of the inversion process for analytical purposes. Wohl modifies the formula of Landolt etc. according to the amount of sugar used for inversion and finds for one-quarter normal weight in 100 cc. the constant —41.7; for one-eighth normal weight in 100 cc. the constant —40.4. Wohl tests the correctness of Clerget's constant in connection with Clerget's process of inversion and finds —43.99 in opposition to the —42.4 found by Professor Ross and his experts. Wohl finds that by dissolving and inverting the half French normal weight in fifty cc. the constant is changed to —44.1, and by dissolving and inverting the German half normal weight in fifty cc. the constant is changed to —44.6. This is in accordance with Gubbe's formula given for the specific rotary power of invert sugar solutions, but it stands in opposition to the results obtained by Professor Ross and his experts. As anybody might surmise from Gubbe's classical treatise† the use of the German half normal weight instead of the French half normal weight would require the employment of a constant higher than Clerget's original constant, and not a constant lower as suggested by Professor Ross and his experts.

For practical analytical purposes Clerget's method of inversion is nearly exclusively used for second products and molasses. By dissolving the German half normal weight of such substances in fifty to fifty-five cc. the concentration of the sucrose liquors is more or less similar to the concentration for which Clerget's original constant was determined. The error arising from applying Clerget's constant in connection with the German half normal weight is thus almost eliminated for the purposes mentioned above.

* Zeitschrift für [illegible] 98, [illegible]

† Ber. d. chem. [illegible]

2. The other argument brought up by Professor Ross is: "So that the substitution of a new constant for the 144 of Clerget is not a new departure, especially where somewhat different conditions obtain. At any rate it is at least certain that 'all the chemists in the sugar industry' do not use Clerget's original formula, as Mr. Breyer would have the readers of your journal infer." We think that Professor Ross' attempted protection of the readers of this journal from such inferences is quite out of place. No one who notices that we mention in our first article Landolt's figure 142.4, Creydt's 142, and Herzfeld's 142.66 will think us unaware that different constants are used for analytical determinations of that kind. We do not consider the substitution of a new constant a new departure, when the conditions of the reaction are modified. But what we do think a new and entirely unjustifiable proceeding is that Professor Ross and his associates substitute a new constant in a method recognized by chemists of the highest standing and leave the conditions of the reaction unchanged, thus insinuating that the original method must give false results. That this was done by Professor Ross and his associates appears clearly from the literature quoted, and if Professor Ross should entertain different views, we ask of him to point out the literary facts which might convince us to the contrary.

3. Professor Ross says further: "As to the low reading of the normal sucrose solution at 4° * * * The results were stated as noted accurately by three observers of experience in polariscopic work and were merely mentioned incidentally along with other data secured and not with the intention of advancing a new theory or opinion with regard to the polarization of sucrose solutions at low temperatures." We are sorry to see that Professor Ross is not aware of the importance of the observation made by himself and three observers of experience in polariscopic work and that he mentions the low readings at 4° C. incidentally only. We beg to differ from Professor Ross also in this point and think that these observations are the most interesting made by himself and his associates on account of their being so very opposite to the results of all the other chemists who ever studied the optical qualities of sucrose solutions. Professor Ross and the three observers of experience in polariscopic work would render

the greatest service to science by a repetition of their experiments and by explaining the startling phenomenon observed in Louisiana.

SEPARATION OF IRON OXID FROM ALUMINA IN PHOSPHATIC ROCKS, BY FUSION WITH ALKALINE CARBONATE.*

BY CHARLES GLASER

In *Zeitschrift für analytische Chemie*, **31**, 4, I have given a method for the determination of alumina in phosphatic material containing both iron and alumina. In this process both metals are precipitated from solution as phosphates, and then are separated by fusion with sodium carbonate. The investigation upon which the process was based justified the statement that the quantity of aluminum phosphate present could be found by deducting from the weight of the phosphates of both bases the ferric oxid present, together with so much phosphoric acid as would be required to form with it ferric phosphate, $FePO_4$.

In the better grades of Florida phosphates the quantity of iron is limited, often not more than 0.25 per cent of oxid being present, while alumina occurs in quantities of from four to eight per cent., and sometimes much more.

Aluminum phosphate, $AlPO_4$, may be precipitated with certainty by the method given in the paper already referred to. Yet it has not heretofore been observed that ferric phosphate seems to suffer a partial decomposition. Since that paper was published, I have had occasion to examine a number of phosphate samples containing iron oxid largely in excess of alumina and below I submit the results of a number of analyses for comparison.

No.	Mixed Phosphates of Iron and Aluminum Found	Oxid of Iron found	Phosphate of Iron calculated	Phosphate of Aluminum found	Alumina calculated	Phosphates of Iron and Aluminum calculated	Difference
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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* The Pharmaceutical Review, October, [illegible]

The mixed phosphates were obtained by repeated precipitation with ammonium acetate, adding some sodium phosphate to insure excess of phosphoric acid, with the exception of Nos. 4 and 5, where the sodium phosphate was omitted. This accounts for the larger discrepancy, as in the absence of an excess of phosphoric acid the tendency to form basic salts is very pronounced. But even when sodium phosphate has been employed, as the above table shows, the weight of the mixed phosphate is less (on the average about 0.61 per cent., leaving out the extremes Nos. 4 and 5), than called for by the respective amounts of the oxids estimated.

In order to verify the determination of ferric oxid, this was determined in sample No. 7 by two titrations with potassium permanganate, the results being 4.56 and 4.52 per cent. respectively.

I have as yet not been able to ascertain the conditions under which the mixed phosphates of aluminum and iron can be precipitated exactly as of the formula MPO_4, and I would, therefore, recommend for the present that the aluminum be determined as phosphate, $AlPO_4$, held in solution by sodium carbonate, after separation of ferric oxid.

To facilitate matters I will repeat the method of separation in detail. The hydrochloric acid solution of a phosphorite is nearly neutralized with ammonia, using methyl orange as an indicator; ammonium acetate is now added until the color changes completely from red to pale yellow—it is advisable to use a slight excess. Place the beaker containing the mixture in a water bath at a temperature of not over 70° C. until complete separation of the aluminum and iron phosphates has taken place; the precipitate is collected on a filter and thoroughly washed with water of not over 70° C. temperature by means of a filter pump. In this way precipitation of the lime salts is avoided, but as a slight quantity is likely to be retained mechanically by the phosphates, it is advisable to redissolve the precipitate in dilute hydrochloric acid, and precipitate again in the manner above stated, first, however, adding a little sodium phosphate to the solution.

After complete washing the mixed phosphates are heated in a tared platinum crucible, care being taken, however, that the temperature does not rise so high as to cause fusion of the iron

phosphate. When incineration of the filter has been completed, the mass is weighed and then covered with chemically pure sodium carbonate or bicarbonate; the mixture is fused for about ten minutes over a blast lamp, allowed to cool and the crucible then placed in a beaker containing a little water—after moistening the fusion the beaker is heated until the water boils. It will now be found that the cake can be removed easily from the crucible and transferred to the boiling water in the beaker without loss; the crucible should be well rinsed and set aside for further treatment in case it shows traces of adhering ferric oxid. The contents of the beaker are boiled until everything except the oxid of iron is dissolved, then filtered hot and the residue carefully washed with boiling hot water. The ferric oxid on the filter and any remaining in the crucible is now dissolved in hydrochloric acid, and re-precipitated by ammonia, filtered, washed, ignited, and weighed in the usual manner. If the process has been carefully conducted it will be free from phosphoric acid and alumina.

To the filtrate from the fusion which contains everything except the iron, hydrochloric acid is added to expel carbon dioxid and then ammonium acetate, as described before, to precipitate alumina as aluminum phosphate.

In spite of the little extra labor necessitated by the [illegible] it is considerably shorter than any other yet proposed [illegible] at the same time very accurate results.

TENTH ANNUAL REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee notes with satisfaction a growing appreciation of the Reports on Chemical Bibliography that have been presented to the Chemical Section of the American Association for the Advancement of Science. The Ninth Annual Report was widely circulated, appearing not only in the *Proceedings of the American Association for the Advancement of Science*, but also in the *Chemical News*, the JOURNAL OF ANALYTICAL AND APPLIED

* [illegible] *Proceedings of the American Association for the Advancement of Science*, [illegible]

CHEMISTRY, the *Journal of the American Chemical Society*, and the *Scientific American*.

The Committee congratulates the Section on the fact that these annual reports have in large measure accomplished one of the principal objects sought, *viz.*, that of directing attention to the importance of compiling bibliographies, catalogues, and indexes to the voluminous literature of chemistry. While little systematic work has been undertaken, duplication of labor has been prevented and independent efforts have accomplished much; how much appears in the list of bibliographies forming the appendix to this report. Chemists are more and more perceiving the advantages of attaching carefully prepared bibliographies to their monographs. Recently this plan has been pursued in the important *Bulletins* of the Chemical Division of the United States Department of Agriculture. Thus a collection of special bibliographies is gradually forming, destined to be of inestimable value to the chemist. The committee expresses the hope that this collection will grow in the future much faster than in the past, and suggests that members of the Section of Chemistry seriously consider in what way they can individually contribute to the cause.

During the current year the following indexes have been published:

1. A Bibliography of the Electrolytic Assay of Copper. By Stuart Croasdale. In J. Annal. Appl. Chem., 5, 133 and 184 (Mar. and Apr., 1891).

2. An Index to the Literature on the Estimation of Nitrogen by Kjeldahl's Method and its modifications. By Lyman F. Kebler. In J. Anal. Appl. Chem., 5, 260 (May, 1891). [Contains numerous errors, see p. 540.]

3. An Index to the Literature on the Estimation of Nitrogen by all other Methods. By Lyman F. Kebler. In J. Anal. Appl. Chem., 5, 264 (May, 1891). [Contains numerous errors, see p. 540.]

4. Index to the Literature of the Tannins. By Professor Henry Trimble, Ph.M., of Philadelphia. This forms an appendix to "The Tannins: a Monograph on their History, Preparation, Properties, Methods of Estimation, and Uses of the Vegetable Astringents," by the author named. Philadelphia, 1892, Vol. 1, 168 pp., 12mo. The Index occupies pp. 101–165, and the titles are arranged chronologically with an alphabetical index of authors. The whole is admirably printed and obviously exhaustive.

5. Index to the Literature of Angelic and Tiglic Acids from 1842–91. By Henry P. Talbot, Ph.D. Technology Quarterly, 5, Nos. 1 and 2 (Massachusetts Institute of Technology, Boston). Contains an historical summary, and author and subject indexes.

6. Bibliography of Analytical and Applied Chemistry for the year 1891. By H. Carrington Bolton. J. Anal. Appl. Chem., 6, 61, 1892.

We chronicle also the following contributions to chemical bibliography:

7. Professor Thomas B. Stillman, in his papers on "Animal Marine and Vegetable Oils used in Lubrication," has paid especial attention to the bibliography of the subject, grouping under each division of his essay many references to periodical and other literature. J. Anal. Appl. Chem., 5, April, June, and December 1891.

8. A list of chemical synonyms is found in pages [illegible] of the Appendix to "The Scientific American Cyclopedia of Receipts, Notes and Queries." Edited by Albert A. Hopkins. New York, 1892. 8vo. Ill.

9. Prof. Samuel P. Sadtler's "Handbook of Industrial Organic Chemistry." Philadelphia, 1891, pp. xiv-519, roy. 8vo. Ill.) contains bibliographies at the close of each chapter embracing the following topics:

1. Petroleum and Mineral Oil Industry
2. Industry of the Fats and Fatty Oils
3. Industry of the Essential Oils and Resins
4. The Cane and Sugar Industry
5. The Industries of Starch and Its Alteration Products
6. Fermentation Industries (Malting, Brewing, Wines, Spirits, Vinegar, Flour and Bread)
7. Milk Industries
8. Vegetable Textile Fibers and their Industries
9. Textile Fibers of Animal Origin
10. Leather, Glue and Gelatin
11. Destructive Distillation Industries
12. Artificial Coloring Matters
13. Natural Dye Colors
14. Bleaching, Dyeing and Textile Printing

The bibliographies are chronologically arranged, some hundreds.

Professor S. F. Peckham reports substantial progress on his Bibliography of Bitumen; Professor Arthur M. Comey on his Dictionary of Solubilities; and Dr. Alfred Tuckerman on his Bibliography of Mineral Waters. Dr. Arnold Eckart of New York, has completed the manuscript of an Index to the Literature of Stereochemistry; this will appear as an appendix to his review of the subject in the *American Chemical Journal*. The whole will also be issued independently. Prof. Chas. F. Mabery announces Part II of his Index to the Literature of Explosives, to be published shortly. Dr. H. C. Bolton's Select Bibliography of Chemistry has been accepted by the Smithsonian Institution for its Miscellaneous Collections and is in the hands of printers.

H. CARRINGTON BOLTON, *Chairman*.
F. W. CLARKE.
ALBERT R. LEEDS.
ALEXIS A. JULIEN.
JOHN W. LANGLEY.
ROBERT B. PRESCOTT.
ALFRED TUCKERMAN.

APPENDIX TO TENTH ANNUAL REPORT OF COMMITTEE ON INDEXING CHEMICAL LITERATURE.

LIST OF INDEXES TO CHEMICAL LITERATURE.

Abbreviations of Titles of Chemical Journals. By H. Carrington Bolton (and others). J. Anal. Chem., 2, pt. 1. Jan., 1888.

Amalgams; Index to the Literature of. By William L. Dudley, in his Vice-Presidential Address to the American Association for the Advancement of Science, at Toronto. Proceedings A. A. A. S. for 1889, pp. 161-171, 1890. 8vo.

Ammonia from Atmospheric Nitrogen, An Index of Researches upon the Production of. By Ezra J. Ware. Published in Proceedings Michigan State Pharmaceutical Association, 1888. H. J. Brown, Secretary, Ann Arbor, Mich.

Analytical Chemistry, Bibliography of, for the year 1886. By H. Carrington Bolton. J. Anal. Chem., 1, pt. 3. July, 1887.
The same for 1887. *Idem.*, 2, pt. 1. Jan., 1888.
The same for 1888. *Idem.*, 3, pt. 4. Oct., 1889.
The same for 1889. *Idem.*, 4, pt. 1. Jan., 1890.
The same for 1890. *Idem.*, 5, No. 3. March, 1891.

Analytical and Applied Chemistry, Bibliography of, for the year 1891. By H. Carrington Bolton. J. Anal. Appl. Chem., 6, 61, 1892.

Angelic and Tiglic Acids, Index to the Literature of. By Henry P. Talbot. Technology Quarterly, Boston, 5, Nos. 1 and 2, 1892.

Beeswax and Waxes used in adulterating Beeswax, Bibliography of. By Harvey W. Wiley [Editor]. Foods and Food Adulterants. Part VI. Bulletin No. 13, Division of Chemistry, U. S. Department of Agriculture, Washington, 1892, 8vo, pp. 886-871.

Butines and their Halogen Addition Products, Index to the Literature of the, 1863-1888. By Arthur A. Noyes. Technology Quarterly, Boston, December, 1888. Published at the Massachusetts Institute of Technology.

Butter, Bibliography of. By Elwyn Waller. In Second Annual Report of the New York State Dairy Commissioner, 1886.

Chemistry, A Bibliography of, for the year 1883, by H. Carrington Bolton. In "An Account of the Progress of Chemistry in the Year 1883." Smithsonian Report for 1883. Washington, 1884. 8vo.
The same for 1884, 1885, 1886, in Smithsonian Reports for said years.

Chemistry, A Bibliography of, for the year 1887. By H. Carrington Bolton. Washington, 1888. Smithsonian Miscellaneous Collections, No. 665, 13 pp., 8vo.

Columbium, Index to the Literature of. 1801-1887. By Frank W. Traphagen. Smithsonian Miscellaneous Collections, No. 663. Washington, 1888. Pp. iv-27. 8vo.

Copper, Electrolytic Assay, Bibliography of. By Stuart Croasdale. J. Anal. Appl. Chem., 5, 133 and 184. 1891.

Electrolysis, Index to the Literature of. 1784-1880. By W. Walter Webb. Annals of New York Academy of Sciences, 2, No. 10. 1882. Pp. 44, 8vo.
N. B. This has been translated into French by Donato Tommasi, Paris, 1889.

Explosives, Index to the Literature of. Part 1. By Charles E. Munro, Baltimore, 1886. Pp. 42, 8vo. Part II, in press (1892).

Food Adulteration and its Detection, Bibliography of. By Jesse P. Battershall. In "Food Adulteration and its Detection." New York, 1887. 8vo.

Geometrical Isomerism, A Bibliography of. Accompanying an Address on this subject to the Chemical Section of the American Association for the Advancement of Science, at Indianapolis, August, 1890. By Robert B. Warder. Proceedings A. A. A. S., Vol. XXXIX, Salem, 1890, 8vo.

Heat, Dictionary of the action of heat upon certain metallic salts, including an Index to the principal literature upon the subject. Compiled and arranged by J. W. Baird. Contributed by A. B. Prescott, New York, 1884. Pp. 70, 8vo.

History of Chemistry, Outlines of a Bibliography of the. By H. Carrington Bolton. Ann. Lyc. Nat. Hist. Vol. X, pp. 352–361 New York, 1873.

Honey, Bibliography of. By Harvey W. Wiley (Editor). Food and Food Adulterants, Part VI. Bulletin No. 13. Division of Chemistry, U. S. Department of Agriculture, Washington, 1892. 8vo., pp. 871–874.

Iridium, Bibliography of the Metal, by Nelson W. Perry in Prof. W. L. Dudley's paper on Iridium, published in Mineral Resources of the United States, calendar years 1883 and 1884. Washington, 1885. 8vo.

Light, Chemical Influence of, A Bibliography of. Alfred Tuckerman. Smithsonian Miscellaneous Collections, No. 785, Washington, 1891. Pp. 22, 8vo.

Manganese, Index to the Literature of. 1596–1874. By H. Carrington Bolton, Annals of the Lyceum of Natural History, New York. Vol. XI, November, 1875. Pp. 44, 8vo.

Milk, Bibliography of. By Edward W. Martin. In Second Annual Report of the N. Y. State Dairy Commissioner. 1886.

Nitrogen, Estimation of, by Kjeldahl's method. Index to the Literature. By Lyman F. Kebler. J. Anal. Appl. Chem., 5, 260, 1891.

Nitrogen, Fixation of Atmospheric. For bibliographical data see Historical Summary on this subject by A. A. Breneman in J. Am. Chem. Soc., XI, 1889.

Ozone, Index to the Literature of. 1875–1879. By Albert R. Leeds. Annals of the New York Academy of Sciences. Vol. I, No. 12, 1880, pp. 32, 8vo.

Ozone, Index to the Literature of, 1879–1883; accompanied by an Historical, Critical Resumé of the Progress of Discovery since 1879. By Albert R. Leeds. Annals N. Y. Academy of Sciences, Vol. III, p. 137. 1884, pp. 16, 8vo.

Periodicals, A Catalogue of Chemical. By H. Carrington Bolton. Annals N. Y. Acad. Sci. Vol. III, pp. 159–216. New York, 1885, 8vo. Also, Chem. News Print, London, 1886, 12mo.

Supplement to the same. Ann. N. Y. Acad. Sci., Vol. IV, Feb. 1887, 4 pp., 8vo.

Periodicals, Short Titles of, current in 1887. By H. Carrington Bolton. J. Anal. Chem., Vol. I, part 1, 1887, 4 pp., 8vo.

Peroxid of Hydrogen, Index to the Literature of, 1818–1878. By Albert R. Leeds. Annals of the New York Academy of Sciences, Vol. I, No. 13, 1880, pp. 11, 8vo.

Peroxid of Hydrogen, Index to the Literature of. 1879–1883. By Albert R. Leeds. Annals of New York Academy of Sciences, Vol. III, p. 153, 1884, pp. 3, 8vo.

Petroleum, A Bibliography of. By Prof. S. F. Peckham. Report on the Production, Technology, and Uses of Petroleum and its Products. Report of the Census of the United States. Vol. X, 1884, 4to, pp. 281–301.

Ptomaines, A Bibliography of. Accompanies Victor C. Vaughan's Ptomaines and Leucomaines. Philadelphia, 1888, pp. 296–314, 8vo.

Speed of Chemical Reactions, Literature of. By Robert B. Warder. Proc. A. A. A. S. Vol. XXXII, 1883, pp. 3, 8vo.

Specific Gravity of Solids and Liquids, A Table of. The Constants of Nature, Part I (new edition, revised and enlarged). By Frank Wigglesworth Clarke. Washington, 1888. Smithsonian Miscellaneous Collections, No. 659, pp. xi–409, 8vo.

Spectroscope, Index to the Literature of. By Alfred Tuckerman. Smithsonian Miscellaneous Collections, No. 658. Washington, 1888, pp. x–423, 8vo.

Starch-Sugar, Bibliography of. By Edw. J. Hallock. Appendix E to Report on Glucose prepared by the National Academy of Sciences, in response to a request made by the Commissioner of Internal Revenue. U. S. Internal Revenue, Washington, D. C., 1884, pp. 44, 8vo.

Tannins, Index to the Literature of. By Henry Trimble. The Tannins. Philadelphia, 1892. Vol. I, Appendix.

Tea, Coffee, and Cocoa Preparations, Bibliography of the Literature on. By Guilford L. Spencer. Food and Food Adulterants. Part VII, Appendix A. Bulletin No. 13, Division of Chemistry, U. S. Department of Agriculture. Washington, 1892. 8vo, pp. 991–1009.

Thermodynamics, Index to the Literature of. By Alfred Tuckerman. Smithsonian Miscellaneous Collections, No. 741. Washington, 1890, pp. vi-329, 8vo.

Titanium, Index to the Literature of. 1783-1876. By Edw. J. Hallock. Annals of the New York Academy of Sciences. Vol. I, Nos. 2 and 3, 1877, pp. 22, 8vo.

Uranium, Index to the Literature of. By H. Carrington Bolton. Annals of the New York Lyceum of Natural History, Vol. IX, February, 1870. 15 pp., 8vo.

Uranium, an Index to the Literature of. 1789-1885. By H. Carrington Bolton. Smithsonian Report for 1885. Washington, 1885, pp. 36, 8vo.

Vanadium, Index to the Literature of. By G. Jewett Rockwell. Annals of the New York Academy of Sciences, Vol. I, No. 5, 1877, pp. 32, 8vo.

INDEX TO AUTHORS.

THE ANALYSIS OF THE BARIUM GROUP.*

BY B. C. HESSE.

In a communication to the St. Louis Academy of Science, Dr. C. Lüdeking reports the results of experiments which he has performed to test the accuracy of the present methods now in

* Translated from the *Pharmaceutische Rundschau*, April, 1892.

use for the analysis of the Barium Group. His conclusions are:

1. The limit of the gypsum reaction for barium as chlorid, is one part barium chlorid to one thousand parts water.

2. For the dichromate reaction the limit is one part chlorid to 3,333 parts water.

3. The gypsum reaction for barium is so imperfect, that under certain conditions, 0.5 per cent. of barium chlorid may be overlooked.

4. The dichromate reaction is not so much influenced by calcium salts.

5. The limit of the gypsum reaction for strontium as chlorid is one part to 1,666 parts water.

6. Calcium salts have far more prejudicial influence upon the detection of strontium. Under certain conditions 0.9 cent. strontium chlorid may be overlooked.

7. A solution containing thirty per cent. $SrCl_2$, $6H_2O$. reacts like barium with gypsum solution.

8. Strontium salts hinder the gypsum reaction with barium but have no influence upon the dichromate reaction.

9. The method which involves the use of gypsum in distinguishing between barium and strontium should not be employed.

To replace this the following method is recommended: The carbonate precipitate is dissolved in acetic acid, and the barium precipitated with dichromate. In the filtrate strontium and calcium are precipitated as carbonates, redissolved in hydrochloric acid, the calcium detected as oxalate and the strontium spectroscopically.

Since conclusions 1 and 8 were drawn from hydrochloric acid solutions, it seemed desirable to study the behavior of these metals in acetic acid solution. For this purpose the following experiments were performed.

1. *Delicacy of the Gypsum and Dichromate Reactions in Acetic Acid Solutions.*—This was found to be for gypsum one part barium acetate to 13,850 parts water, and for dichromate one part acetate to 27,700 parts water.

These results compare with those obtained by Lüdeking as follows:

	Barium chlorid.	Barium acetate.
With gypsum	1 : 1,538 water	1 : 25,812 water
With dichromate	1 : 5,128 "	1 : 51,624 "

2. *Influence of Calcium Salts.*—

Ba solution.	Ba : Ca	$CaSO_4$.	$K_2Cr_2O_7$.
1 : 28,683	1 : 673		No turbidity in 2 hours.
1 : 12,900	1 : 302	No turbidity in 80 minutes.	Strong turbidity in 30 seconds.
1 : 8,600	1 : 272	Slight turbidity in 30 minutes.	Instantaneous turbidity and formation of sediment in the cold.
1 : 5,176	1 : 121	In 11 minutes a slightly turbid liquid which gives no precipitate in 50 minutes.	Instantaneous precipitation.

The proportion between the volume of the gypsum solution and the solution to be examined was 1 : 10, and even if this proportion was 1 : 2, no increase in delicacy was observed as is the case with strontium.

3. *Influence of Strontium Salts.*—These salts do not lessen the delicacy of the dichromate reaction, but more time must elapse than when barium alone is present. The gypsum reaction was always doubtful. In a test experiment in which the solution contained one part strontium acetate to twenty-seven parts water, gypsum solution gave a precipitate in the cold after three minutes, while the same solution gave with dichromate no reaction after forty-eight hours and after ninety-six hours a very insignificant turbidity.

4. *Delicacy of the Gypsum Reaction with Strontium.*—In these experiments it was clear that the volume of gypsum solution used was of importance.

Gypsum sol.	:	Strontium sol.	Delicacy of the reaction.
1	:	10	1 : 322
1	:	2	1 : 5,316
1	:	1	1 : 8,050
2	:	1	1 : 8,050

5. *Influence of the Calcium Salts upon the Gypsum Reaction for Strontium.*—This influence is very considerable, so that under certain conditions one part strontium in 536 parts of water may be overlooked.

It is evident from these experiments that the method of Dr. Lüdeking is far more delicate than his own results indicate.

A method for the separation of small amounts of strontium from large amounts of calcium is still lacking. The author hopes soon to communicate the results of experiments having this in view.

THE SPELLING OF CHEMICAL WORDS

By Edward Hart

Man is naturally a conservative animal and does things in a certain way because he is accustomed so to do them. This conservatism usually increases with age until it becomes almost impossible to shake it off.

Chemists, however, as a class, have always been noted for their progressive and liberal ideas. New methods, if good are sure of immediate acceptance and use. In very few of the professions have the metric system and the centigrade scale found such universal acceptance; and although a few of our English brethren still reckon in grains they are in a small and decreasing minority.

It is not surprising then that the proposed reform in the spelling of some chemical words should have found so many willing to change the habits of a lifetime and adopt new methods. There are still a few, however, who apparently do not understand the reasons for the changes proposed and therefore hesitate to adopt them. For such, a few words of explanation may not be out of place.

A list of the more important changes proposed and the reasons therefor are given below. This list was written at my request by Prof. T. H. Norton, the Chairman of the Committee. Prof. Norton writes as follows concerning it

Dear Prof. Hart

I have just returned to Cincinnati and find your favor of August [illegible] cheerfully comply with your request and enclose the accompanying list of the more important features of the changes recommended by our committee with brief statements of the reasons. Please feel at liberty to alter, omit or augment as you deem best. I feel that we made a mistake in not appending to our final report some such brief resumé of reasons. As it stands it has somewhat of a bald arbitrary look. As you have already found by experience and I have likewise observed [illegible] at Rochester but a small number of chemists have been able to follow [illegible] of our work.

A LIST OF THE MORE IMPORTANT CHANGES IN THE SPELLING AND PRONUNCIATION OF CHEMICAL TERMS, RECOMMENDED BY THE A. A. A. S., WITH THE REASONS THEREFOR

ELEMENTS

Aluminum is spelled in the shortened form in deference to the wishes of technical chemists on account of the growing importance of the metal in manufactures.

Cesium loses the *a* of the diphthong, as unnecessary, while the new form is in harmony with the French and Italian orthography.

Columbium replaces *Niobium* as a matter of historical justice. It seems important that the one element discovered and named by an American chemist should retain its original patriotic appellation.

Glucinum is preferred to *Beryllium* on the same ground of historical priority.

Sulfur is modified in accordance with the general phonetic simplification going on in our language. The new form brings us into accord with the French, German, and Italian usage. The replacement of **ph** by **f** is carried out in all the derivatives. (It has not been deemed advisable to yield at present to the wish of many that a similar change should be made in the spelling of phosphorus, as the German and French languages still retain the **ph.**)

The termination **-ic.**—This is used for metals only when there is a contrast with **-ous,** thereby avoiding several non-euphonious terms, and bringing us into accord with the British custom. Thus avoid aluminic,, zincic, strontic, etc.

The termination **-ol.**—This is used exclusively for alcohols, and all alcohols receive the termination. This also is in harmony with British usage and brings about a most desirable simplification and uniformity. Thus, glycerol, quinol, etc.

Terminations in **-id.**—The final **e** is dropped from all chemical terms formerly ending in **-ide**, and the pronunciation is always -ĭd. Of the three pronunciations of this termination— -ĭde, -ĭde, and -īde—in varying degrees of use amongst us, the second appeared undoubtedly the most preferable for the following reasons: -ĭde is an uncommon, almost unnatural pronunciation of the vowel in our language, although it would bring us into unison with European usage and simplify phonetic values for the

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Fāte, făt, fär, mēte, mĕt, pīne, pĭn, marĭne, nōte, nŏt, möve, tūbe, tŭb, rüle, mȳ, ȳ = ĭ.

' Primary accent; " secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

ears of foreigners; -ide leads frequently to confusion with -ite (sulfide and sulfite) and is the value of i farthest removed from European usage; -id approximates closely to the continental i, —into which it is easily lengthened,—is readily recognized by the foreign ear, is not confused with the termination -ite, is in line with present phonetic progress, and has the backing of authority and usage. The short sound of i naturally dictates the dropping of the final e. (According to Smart and Cull, chemical terms ending in **-ide**, as bromide, chloride, etc., should be pronounced with i long; but all other orthoepists are unanimous in making the vowel short; and the propriety of the latter mode of pronunciation is established by the fact that this whole class of words is not unfrequently spelt without the final e: thus bromid, chlorid. Webster's Dictionary, edition of 1864 and 1884. Principles of Pronunciation, p. xliv.)

Terminations in **-in.**—In the names of chemical compounds, including all those formerly ending in **-ine** (except the small group of doubly unsaturated hydrocarbons, as propine) this termination is always pronounced -in and is never followed by an e. In this case much the same reasons as those given in the preceding paragraph dictate the uniform use of -in, and not only authority, but modern usage, is even more fixed in the employment of the short i, so much so that the change practically amounts to simply dropping the final -e when following -in. The only objection to be raised against the innovation is that based upon the recommendation of Watts some few years since that basic substances should terminate in **-ine** and neutral substances (i.e., glycerids, glucosids, proteids, and bitter principles) in **-in.** While this distinction possesses a certain value it is to be noted that it involves a difference in spelling with little or no difference in pronunciation—a useless and undesirable complication and out of touch with modern phonetic principles; it demands a very extensive knowledge of the constitution of a large number of compounds with these terminations; it has never been recognized by many chemists, and finally while it has been partially adopted by others it has rarely been used consistently.

Terminations in **-meter.** Words in this class used in the

metric system are regarded as compound words, and each portion retains its own accent; as mil'lime"ter. Of the two authorized forms of accentuation, it was deemed better to retain this and exclude completely the other (*viz.*, the uniform laying of the accent on the antepenult), because the former is of help to foreigners using our language and *vice versa*, while the practice accords with the general rule for the retention of the primitive accents in compound words.

Derivatives of Valence.—The Latin prefixes are used invariably to the exclusion of the Greek, in accord with the recognized principles of word-building in our language.

Arsin, *Stibin*, *Phosphin*, *Hydrogen Sulfid.*—These shorter terms, long since adopted by many chemists, now supersede completely the cumbersome arsenetted hydrogen, etc. (It is to be hoped that the simplication may soon be carried a step further by the introduction of sulfin, selenin, and tellurin.)

Gramme.—The retention of the **-me** of the French spelling may seem to ill accord with principles of phonetic reform actuating many of the above changes. It is, however, dictated by reasons of prudence, as long as the metric system is used side by side with the old apothecaries' series of weights and measures by our physicians and pharmacists. When the transition period is over, and the latter system is effectually displaced, the simpler form will unquestionably be adopted. It is obvious to all that the marked similarity in sound and spelling between the words *grain* and *gram* could easily lead to mistakes of the gravest nature, and as a matter of fact a number of deaths have already been caused by either mere inadvertence or by the omission of the dot over the *i* in *grain*. (*Amer. Druggist*, **20**, 369.)

These proposed changes were carefully canvassed with those gentlemen who have made the English language their life study and who were unanimously in favor of them. They were made the subject of a number of reports to the American Association for the Advancement of Science and were favored by a large majority of those present. In drawing up the report the committee sought and obtained the opinions of a number of chemists not members of the Association and so far as it was possible to

obtain an expression of opinion the recommendations were the wish of American chemists.

The report of the committee was not intended to settle the matter forever. It seems proper however that it should be used as a first step in the right direction. We have long ago dropped the *u* in *favor*, *honor*, *mold*, *etc.*, the redundant *me* in *program* changed *litre*, *centre*, *etc.*, to *liter*, and *center* and in other ways improved and strengthened our language. Let us not hesitate to make other changes when the time comes.

That these changes will please George W. Smalley, who objects to Websterian spelling, or Charles A. Dana who sees no manner of reason in spelling reform is hardly to be expected. In the July number of Harpers Magazine, Brander Matthews has however, shown in a most convincing manner the weakness of such objections. The article should be read in full. For those who cannot do this the following extracts will be of interest.

"The most of those who write with ease in British journals deploring the prevalence of 'American Spelling' have never carried their education so far as to acquire that foundation of wisdom which prevents a man from expressing an opinion on subjects as to which he is ignorant. * * Now literature is one of the arts and philology is a science. Though men of letters have to use words as the tools of their trade orthography is none the less a branch of philology, and philology does not come by nature.

"As I have said before, the alleged American spelling differs but very slightly from that which prevails in England. A wandering New Yorker who rambles through London is able to collect now and again evidences of orthographic survivals which give him a sudden sense of being in an older country than his own. I have seen a man whose home was near Gramercy Park stop short in the middle of a little street in Mayfair and point with ecstatic delight to the strip of paper across the glass door of a bar proclaiming that *CYDER* was sold within. I have seen the same man thrill with pure joy before the shop of a tailor in the window of which *corduroys* were offered for sale. And this same New Yorker was carried back across the years when he noted the extra *u* in the British *colour*, an orthographic fifth wheel if ever there was one; he smiled at the *e* which

lingers at the end of the British *almanack;* he wondered why a British house should have *storeys* when an American house has *stories;* and he disliked intensely the wanton *e* wherewith British printers have recently disfigured *form*, which in the latest London typographical vocabularies appears as *forme*. This *e* in *form* is a gratuitous addition, and therefore contrary to the trend of spelling reform, which aims at the suppression of all arbitrary and needless letters. Most of the American modifications of the Johnsonian orthography have been labor-saving devices, like the dropping of *u* in *color* and of one *l* in *traveler*, in an effort at simplification, and in accord with the irresistible tendency of mankind to cut across lots."

That the changes proposed by the committee have met with favor is evident from their use in the new Standard Dictionary, now in preparation edited by Dr. F. A. March and published by Funk and Wagnalls of New York City. Dr. Witthaus has adopted them in his *Manual of Chemistry*, Dr. G. C. Caldwell, President of the American Chemical Society, in his *Elements of Chemical Analysis*, reviewed in this issue, as also the late Dr. T. Sterry Hunt, in his *Systematic Mineralogy*.

The changes proposed will also be used in this journal with a single exception. On reflection the reason given for spelling *gramme* does not seem sufficient. The spelling *gram* is already in nearly universal use. If physicians are afraid to spell it *gram* they should add the **-me** until the use of the grain shall have been discontinued. In the meantime, chemists may continue to spell it *gram* to their great advantage.

This is, however, a free country, and no law is likely to be enacted forcing chemists to spell *à la committée*. Neither will the editor of this journal undertake to dictate to chemists in the matter of spelling. Contributors who wish to spell in the old way should, however, so state on the manuscript in order that no misunderstandings may arise.

NEW BOOKS.

Caldwell's Chemical Analysis.*—This book was written, as

*Elements of Qualitative and Quantitative Chemical Analysis. By G. C. Caldwell, Professor of Analytical Chemistry in Cornell University. Second edition, revised and enlarged. Philadelphia: P. Blakiston, Son, and Company. Pp. viii-175.

the author states in the Introduction, for beginners in analysis who do not wish to qualify themselves as chemists and who do not feel able to buy the larger works. The needs of the students in Cornell University are of course first in the writer's thoughts.

Part I opens with a chapter on Solution and Solids from Solution. Then follow chapters on Acids, Bases, Salts; Oxidation; Chlorination, Reduction; Metathesis; Writing Equations; The Manipulations of Analytical Chemistry.

Part II contains chapters on The Mode of Procedure in General; The Preparation of the Solution of the Substance; The Acidigens or Acids; The Analysis for the Acidigens; Basigens or Metals.

Part III contains chapters on The Balance and its Use; Measurement in Volumetric Analysis; Seven Important Operations of Quantitative Work (solution, precipitation, filtration; filtration by suction, washing precipitates, the asbestos filter; preparation of the precipitate for weighing, calculation of the results of the analysis); Miscellaneous Matters (comprising methods for the determination of specific gravity, use of platinum ware; the quantitative note book, miscellaneous maxims).

Part IV comprises The Determination of Iron and of Sulphur Trioxid; Acidimetry and Alkalimetry; The Determination of Lead, Phosphorus Pentoxid, and Calcium; Iodometry; Determination of Antimony; Analysis by Electrolysis; Separation and Determination of Silver and Copper.

Part V contains lists of apparatus and reagents, specific gravity and other tables, and an index.

Altogether the book is the best of its kind that we have seen. Throughout the book the spelling of words recommended by the committee of the American Association for the Advancement of Science has been used.

ERRATA.

The attention of the Editor has been called to numerous errors in the Bibliographies of Nitrogen contained in L. F. Kebler's paper in the number of this Journal for May [illegible], 1895. Those who make use of these bibliographies should therefore verify the references and not take them at second hand.

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METHODS OF SOIL ANALYSIS.

BY DAVID O'BRINE.

There are three methods of soil analysis in common use: (1) The method described in Chemical Bulletin No. 10, United States Department of Agriculture, by Edgar Richards, "Principles and Methods of Soil Analysis"; (2) The method described in Chemical Bulletin No. 31, pp. 233 to 241; (3) The method worked out by Drs. Robert Peter and E. W. Hilgard for the soils of the Southern and Pacific States for the tenth United States Census. It is natural to expect quite an agreement in most things, yet there are many little details that differ widely. Having occasion to use the method of Drs. Peter and Hilgard and thinking it might be of interest to the readers of this journal I give below the following working details:

The soil is thoroughly broken up with a rubber pestle and sifted through a sieve of one-half millimeter meshes to obtain the *fine earth* for analysis. This fine earth is exposed to an atmosphere saturated with moisture for about twelve hours at the ordinary temperature (60° F.) of the cellar in which the box should be kept. For this it is placed in a layer of two millimeters thick upon glazed paper on a table in a small covered box (12×9×8 inches) in which there is about an inch of water; the interior, sides, and cover of the box may be lined with blotting

paper which is kept saturated with water to facilitate the saturation of the air. After twelve hours the earth is transferred as quickly as possible to a weighed drying tube and weighed. It is then heated in a paraffin bath and the temperature gradually raised to 100° C., and is kept there twenty to thirty minutes (rapidity of raising temperature depending on amount of moisture in the soil), a current of dry air passing continually through the tube. It is then weighed again and the loss in weight gives the *hygroscopic moisture*.

From the drying tube two quantities are weighed out — two to two and one-half grams for general analysis and three to three and one-half grams for phosphoric acid determination.

GENERAL ANALYSIS

1. The weighed quantity of two to two and one-half grams is brought into a small porcelain beaker, treated with eight to ten times its bulk of hydrochloric acid, specific gravity 1.115, and two or three drops of nitric acid, and digested for five days over the water bath. At the end of this time it is evaporated to dryness, first on the water bath and then over the sand bath. By this treatment all the silica is rendered insoluble.* It is then moistened with strong hydrochloric acid and two or three drops of nitric acid, warmed and treated with distilled water, after allowing it to stand a few hours on the water bath, then it is filtered from the insoluble residue, which is strongly ignited and weighed.†

* Here I vary from the method of [illegible] perforated bottom. The bath is [illegible] hot is six tubes with ground glass stopper [illegible] one and one-half inches in diameter and [illegible] fifteen feet of [illegible] filled with distilled water [illegible] filling. The [illegible] the bottles [illegible] them to the boiling point [illegible] to give some comparison [illegible] of Hilgard. [illegible]

† Note: If the [illegible] through the filter can be obtained during the [illegible] determination.

The insoluble residue is next boiled for fifteen to twenty minutes in a concentrated solution of carbonate of soda whereby the soluble silica is separated from the sand and insoluble matter, which is again brought upon the filter and ignited and weighed.

2. The filtrate from the insoluble residue is evaporated to a convenient bulk. In case the filtrate should indicate by its color, etc., the presence of any considerable amount of organic matter it should be oxidized by aqua regia, otherwise there will be difficulty in separating alumina.

3. The filtrate thus prepared is now brought to boiling and treated with ammonia, whereby the iron and alumina are precipitated; it is kept boiling until the excess of ammonia is driven off, and then filtered (Filtrate A).

4. The precipitate of iron and alumina is well washed with boiling water, then removed from the filter to a platinum dish. The small quantity which unavoidably remains on the filter is dissolved with boiling hydrochloric acid; the filter is then added to the alumina or may serve for filtering the alumina subsequently.

5. The precipitate in the platinum dish is dissolved in hydrochloric acid, treated over the water bath with alcoholic potash and allowed to digest for at least one hour. By this means the alumina is brought into solution while the iron is precipitated. The iron is brought on a filter and washed with boiling water (Filtrate B). The iron precipitated is dissolved on the filter by hydrochloric acid, the filter being added to the insoluble residue (See Note 1), and precipitated from the boiling solution by ammonia; it is then filtered off, washed, dried, ignited, and weighed.

Filtrate B containing alumina dissolved in potassium hydroxid is acidulated with hydrochloric acid and a few crystals of potassium chlorate are added to destroy any organic matter from the filters, etc.; with this it is digested for an hour, then neutralized with ammonia and the alumina precipitated by ammonium sulfid; it is allowed to settle for a few hours, then filtered off, washed out with cold water to which a few drops of ammonium sulfid have been added, dried, ignited, and weighed. Or this method may be used: The iron and alumina precipitate (with

filter) is dissolved in a mixture of about five cc. hydrochloric acid and twenty cc. water. Then filter (see Note 1) and make up to 150 cc. Take fifty cc. for the determination of iron and alumina together and fifty cc. for iron alone; keep fifty cc. for reserve. Determine the iron by means of a standard solution of potassium permanganate, after reducing, which is done by evaporating the fifty cc. almost to dryness with strong sulfuric acid, water added, and the solution transferred to a flask and reduced by means of pure metallic zinc in the usual way. The alumina is thus determined by difference.

6. The Filtrate A free from iron and alumina, if too bulky, is evaporated down to about twenty-five cc. unless the soil is a calcareous one, and the *lime* is precipitated from it by neutralizing with ammonia and adding ammonium oxalate. The solution containing the lime should be treated boiling with the ammonia as the precipitate settles much more easily in this case. It is allowed to stand for twelve hours, then filtered off, washed with cold water, and dried (Filtrate C).

By ignition the precipitate is partially converted into the oxide. This is then heated with twice its bulk of powdered ammonium carbonate, moistened with hot water, and exposed to a gentle heat (50° to 80° C.) until all the ammonia is expelled. It is then dried below a red heat and determined as calcium carbonate.

When the amount of lime is at all considerable the treatment with ammonium carbonate must be repeated till a constant weight is obtained.

7. The Filtrate C from the lime is brought into a flask, evaporated down over a sand bath and the ammoniacal salts destroyed with aqua regia (Lawrence Smith's method). From the flask it is removed to a small beaker and evaporated to dryness. This process usually occupies four to five hours. The dry residue is now moistened with nitric acid and the silica present is separated by filtration from the filtrate which should not amount to more than ten to fifteen cc. Sulfuric acid is precipitated by treatment with a very few drops of barium nitrate, both the solution and the reagent being heated to boiling. If the quantity of sulfuric acid is large it may be filtered off after the lapse of four or five hours (Filtrate D). If very small let it

stand twelve hours. The precipitate is washed out with boiling water, dried, ignited, and weighed as such.*

Filtrate D is now evaporated to dryness in a platinum dish, the residue is treated with twice its bulk of crystallized pure oxalic acid, moistened with water, and exposed to gentle heat. It is then strongly ignited to change the oxalates to carbonates. This treatment with oxalic acid must be made in a vessel which can be kept well covered; otherwise, there is danger of loss through spattering. The ignited mass is treated with a small amount of water, which dissolves the alkaline carbonates and leaves the carbonate of magnesia and proto-sesquioxid of manganese behind, and also the excess of barium carbonate. The alkalis, and magnesia, barium, and manganese are separated by filtration into a small platinum dish (Filtrate E), and the residue well washed with water. If the color is green, add a small amount of alcohol to oxidize the manganese which will then remain on the filter and the alkalis in the filtrate.

The residue of magnesia, barium, and manganese is now treated on the filter with hydrochloric acid and the platinum dish is washed with nitric acid (not hydrochloric acid, otherwise the platinum dish will be dissolved by chlorin from the manganese), dissolving any small traces of magnesium, barium, and manganese that may have been left behind.

9. The solution containing the chlorids of magnesium and manganese is now freed from the barium salts by precipitation with sulfuric acid, and the barium sulfate, after settling a few hours, is filtered off. The filtrate is neutralized with ammonia, the resulting small precipitate of iron is filtered off and the manganese precipitated with ammonium sulfid. Allow to stand twelve hours and filter (Filtrate F); wash with cold water, dry, ignite, and weigh as manganic oxid.

10. The Filtrate F from the manganese is now freed from the sulfur of the reagent by acidulating with hydrochloric acid, evaporating down if necessary, and filtering. From the solution thus free from sulfur the magnesia is precipitated by adding an equal amount of ammonia and treating with phosphate of soda.

* Note 2.—Care must be taken in adding the barium nitrate because in such a small concentrated acid solution the excess of barium nitrate will crystallize and does not readily dissolve in hot water.

After standing twelve hours the magnesia may be filtered off washed out with ammoniacal water, dried, ignited, and weighed as magnesium pyrophosphate.

11. The Filtrate E (which should not be more than ten or fifteen cc.), containing the carbonates of the alkalis, is evaporated to dryness and gently fused so as to render insoluble any magnesium carbonate that may have gone through then redissolved and filtered into a small weighed platinum dish containing a few drops of hydrochloric acid to change the carbonates into chlorids, evaporated to dryness, exposed to a temperature below red heat by which the chlorids are thoroughly dried and freed from moisture but not volatilized. These are now weighed and the heating repeated until a constant weight is obtained. The weighed chlorids are now brought by means of a little water to a small porcelain dish, treated with a sufficient quantity of platinic chlorid and evaporated to dryness over the water bath. The dried residue is now treated with a mixture of three parts of alcohol and one part of ether, which dissolves the sodium salt but leaves the potassium platino-chlorid undissolved. This is now brought on a filter, washed with ether and alcohol and when dried the precipitate and filter are brought into a small platinum crucible and exposed to a heat sufficiently intense to reduce the platinum chlorid to metallic platinum and to volatilize the potassa. The reduced platinum is now first washed with acidulated water, then with pure water, then all moisture is driven off and it is weighed. From the weight of the platinum may be calculated the potassium chlorid, and then the oxid corresponding; the difference between the weights of the alkaline chlorids and the potassium chlorid gives the sodium chlorid from which may be calculated the oxid.

PHOSPHORIC ACID DETERMINATION.

12. The weighed quantity of three to five grams is brought into a platinum crucible and ignited, care being taken to avoid all loss by dusting. The loss of weight after ignition gives the amount of chemically combined water and volatile matter.

13. The ignited soil is now removed to a porcelain beaker treated with four to five times its bulk of strong nitric acid

digested for five days, evaporated to dryness, first over the water bath and then over the sand bath, moistened with nitric acid and treated with water. After standing a few hours on the water bath it is filtered off from the insoluble residue and the filtrate is evaporated to a very small bulk (twenty cc.) and treated with about twice its bulk of ammonium molybdate, thus precipitating the phosphoric acid. After standing twelve hours it is filtered off and washed with ammonium nitrate. The washed precipitate is now dissolved on the filter with dilute ammonia. After washing the filter carefully the ammoniacal solution is treated with magnesia mixture by which the phosphoric acid is precipitated. After allowing it to stand twelve hours, it is filtered off, washed in the usual way, dried, ignited, and weighed as magnesium pyrophosphate from which the phosphoric acid may be calculated. The per cent. of phosphoric acid is to be subtracted from that of alumina.

HUMUS DETERMINATION IN SOILS.

About ten grams of the soil is weighed off into a prepared filter. The soil should be covered with a piece of filter paper so as to prevent it from packing when solvents are added. It is now treated with hydrochloric acid from 0.5 per cent. to one per cent. strong to dissolve out the lime which prevents the humus from dissolving in ammonia. Treat with the acid until there is no reaction for lime; then wash out all the acid with water. Dissolve the humus with ammonia, prepared by diluting common saturated ammonia (178 cc. ammonia to 422 water). Evaporate the humus solution to dryness in a weighed platinum dish at 100° C.; cool and weigh, then ignite; the loss of weight gives the weight of humus. The residue from ignition is carbonated with carbonic acid from the carbonic acid generator, heated and weighed, thus giving the ash. It is then moistened with nitric acid and evaporated to dryness. The residue is treated with nitric acid and water, allowed to stand a few hours and the solution filtered from the insoluble residue, which is ignited and weighed, giving the silica. The soluble phosphoric acid is determined from the solution by the usual method. Considerable information can be found in the "Scientific Examination of Soils," by Wahnschaffe. The practical question, "Does the

chemical analysis of a soil convey, to an average farmer any tangible information?" has advocates on both sides. It is not my purpose to discuss the question at the present time.

MANUFACTURE OF VEGETABLE OILS.*

From the remotest antiquity Marseilles has been the emporium not only of the oils of the province, but also of those produced in Italy, Spain, the African coast, Greece, and Turkey.

The olive tree is cultivated in the following departments of France: Alpes-Maritimes, Var, Bouches-du-Rhône, Gard, Hérault, Aude, Pyrénées-Orientales, Vaucluse, Basses-Alpes, Drôme, and Ardèche. A district of 152,250 hectares is taken up with its cultivation. The total production is estimated at [illegible] liters, representing a value of 61,095,000 francs. Of this quantity part is consumed within the district producing the oil, the rest being sent into the interior of France or exported to neighboring countries and the colonies.

The import trade in oleaginous seeds is very considerable, the total quantity of the different kinds imported during the year 1890 being nearly 3,500,000 metric quintals. The exact figures of the different kinds of seeds imported during that year are shown in the following table, which is taken from the official statistics published by the chamber of commerce at Marseilles.

[illegible]

* * * * *

In considering the state and movement of the oil trade at Marseilles account must also be taken of the importation of [illegible] palm, and especially of cotton oils. The first two [illegible]

received from the west coast of Africa and from England, and the latter from England and from the United States, the quantity imported during 1890 being 20,000,000 kilograms.

The most important importation of seeds, etc., consists of peanuts, by far the larger quantity of which arrive shelled, only about one-fifth of the total amount imported having the shells on. This product comès, for the most part, from India and Africa. Afterwards, in order of importance, as shown by the quantity imported, come cocoanuts and palm nuts, sesame from India and Africa, cotton seed, shelled peanuts, cultivated and wild rape seed, sesame from the Levant, and finally linseed.

The official records of this city show that during 1890 there has been an increase of importation as compared with 1889 of sesame from the Levant, shelled and whole peanuts, linseed, cultivated and wild rape seed, cotton seed, poppies, palm nuts, and a few other kinds, principally Niger, while a falling off has been shown in the case of sesame from India and Africa, castor beans, pulgheria, cocoanuts, mowrahs, and a few other kinds. The difference between the increase and diminution in the importation of these various kinds shows a net increase of 232,550 quintals during 1890, as appears in tables herewith, while the amount of seed in warehouses at Marseilles at the end of 1890 exceeded the quantity so stored at the end of 1889 by 43,450 quintals. * * * * *

The method followed in extracting the oil from the various seeds imported at Marseilles, the cost of importation, the uses to which the oils are put, and the use made of the residuum are as follows:

SESAME.

Levant sesame.—This is subjected to three pressings, the seed being cold in the first two, but heated for the third, in order to allow of more oil being extracted. Before being pressed at all the seed is thoroughly triturated, to allow the oil to come away more readily under pressure. In the first pressing from thirty to thirty-two per cent. of oil is obtained, and this oil is sold at from ninety to ninety-six francs per 100 kilograms for table consumption. The seed is now thoroughly triturated again, a little water —about one or two per cent.—being added, and, being again put

under pressure, yields from nine to ten per cent. of oil of a quality slightly inferior to the first, but which is still quite good enough for eating purposes. The price of this oil varies from seventy to seventy-three francs per 100 kilograms. After being removed from the press the seed is once more thoroughly triturated and from two to four per cent. of water is added to it, after which it is heated to a temperature of from 70° to 80° C. The oil that now comes away is of very inferior quality to that obtained by the first two pressings, and in quantity is from ten to eleven per cent. of the weight of seed originally put into the press. This oil is sold at from forty nine to fifty-one francs per 100 kilograms and is used in the manufacture of soap. The residuum is made into oil cakes, which are used for feeding cattle, and are sold at from twelve to thirteen francs per 100 kilograms. The cost of transporting this seed to Marseilles is from ten to fifteen francs per ton of 1,000 kilograms.

Indian and African sesame.—This seed, like the sesame from the Levant, is subjected to three pressings, in the first two of which the seed is cold and in the third heated. The oil yielded in the first pressing is not so great as in the former quality of seed, the amount being from twenty seven to twenty eight per cent. of the weight of seed pressed; and it is greatly inferior in quality, being sold at from sixty-two to seventy five francs per 100 kilograms. It is used, according to quality, either for table purposes or for lamp oil. After being triturated again and having from one to two per cent. of water added, the seed is again pressed and yields from nine ten per cent. of oil of a quality slightly inferior to the first, and which, like it, is destined either for eating purposes or for lamp consumption. This oil is sold at prices ranging from sixty to sixty two francs per 100 kilograms. The seed after being mixed with two to four per cent. of its weight of water and heated to 70 or 80° C. is subjected to the third and last pressure from which eight or nine per cent of oil is obtained which is sold at from forty nine to fifty one francs per 100 kilograms and is used in the manufacture of soap. The residuum is made into oil cakes (tourteaux) which are used for feeding cattle and also as fertilizer. These oil cakes are not quite so good in quality as those formed from the residuum of the sesame from the Levant

They are sold at from eleven to twelve francs per 100 kilograms. The cost of transporting this seed to Marseilles from the countries of its origin is from thirty to thirty-five francs per ton of 1,000 kilograms.

SHELLED PEANUTS.

These nuts are subjected to two pressings, the seed being first triturated and then heated to between 70° and 80° C. It is to be noted that the treatment of this product differs from that to which the sesame is subjected, in that peanuts are not pressed cold at all, but have to be heated even for the first pressing.

The yield of oil arising from the first pressing is about fifty per cent. of the seed crushed. It is used in the manufacture of soap, and also for lubricating purposes, and is sold at the rate of fifty francs per 100 kilograms.

POPPY SEED.

Poppy seed is pressed twice cold and then heated and pressed once more. The seed is first thoroughly triturated, and yields in the first pressing twenty-two per cent. of its weight in oil. This oil is worth seventy-two francs per 100 kilograms, and is used for table purposes and also to a very considerable extent in the manufacture of fine paints. After being crushed a second time and having one or two per cent. of water added, the seed is pressed again, when ten per cent. more oil is obtained, which is used, like the first, for table purposes and for making oil paints, and also for burning. This oil sells at sixty francs per 100 kilograms. The seed being crushed again, mixed with about three per cent. of its weight of water and heated to a temperature of from 70° to 80° C., yields in the third pressing seven per cent. of its weight in oil, which is used almost exclusively in the manufacture of soap, and is sold at fifty francs per 100 kilograms.

The residuum is made into oil cake and is sold at 11 to 11.50 francs per 100 kilograms. This oil cake is used for fertilizing purposes. The cost of shipping this seed to Marseilles is from thirty to thirty-five francs per ton of 1,000 kilograms.

LINSEED.

Linseed is subjected to two pressings, in the first of which the seed is cold and in the second heated. The yield of oil in the

first pressing is twenty-two per cent. of the weight of the seed, and the oil obtained is used for table purposes, being sold at from sixty-two to sixty-three francs per 100 kilograms. After being triturated a second time—it having been triturated as usual before the first pressing—the seed receives the usual addition of about two per cent. of its weight of water, and is heated to a temperature of from 70° to 80° C., and is afterwards again placed in the press, when it yields ten per cent. of its weight in oil of an inferior quality, which is chiefly used in the manufacture of soap. The residuum is made into oil cakes, which are of superior quality to those produced in the pressing of any other kind of seed. They are used for feeding cattle, and are sold at from sixteen to seventeen francs per 100 kilograms. The cost of transporting linseed to Marseilles is from thirty to thirty-five francs per ton of 1,000 kilograms.

CULTIVATED RAPE SEED.

This seed is pressed twice, once cold and once heated. It is in the first place thoroughly triturated. The first pressing yields twenty-two per cent. of oil, which is sold at the rate of sixty-five francs per 100 kilograms, for lamp oil. After being mixed with from two to four per cent. of water and heated to 70° or 80° C., twelve or thirteen per cent. of oil of an inferior quality is extracted, which is used in the manufacture of soap, and is sold at [illegible] francs per 100 kilograms.

Oil cake is made from the residuum, and is sold for feeding cattle at ten francs per 100 kilograms. The cost of importing rape seed at Marseilles from the countries where it is grown is from thirty to thirty-five francs per ton of 1,000 kilograms.

WILD RAPE SEED.

Wild rape seed is triturated and heated before being put under the press. The first pressing results in a yield of about [illegible] per cent. of oil, which is sold for mixing purposes at the rate of fifty-three to fifty-four francs per 100 kilograms. The second pressing, after the usual trituration, addition of two to [illegible] per cent. of water, and reheating to 70° or 80° C., gives [illegible] per cent. of oil in addition, which, being of slightly inferior quality to the oil first obtained, is sold at fifty francs per 100 kilograms, and is used for making soap.

As in the case of most of the other oils mentioned in this report, the residuum goes to make oil cake, which is used as a fertilizer.

This seed does not cost so much for transportation as those hitherto mentioned (sesame from the Levant excepted). It is shipped to Marseilles at a cost varying between twenty and twenty-five francs per ton of 1,000 kilograms.

CASTOR BEANS.

Castor beans are subjected to two pressings, after being first thoroughly triturated. In the first pressing the seed is cold, and the yield obtained is about thirty per cent. of the weight of the seed. This oil, which is used extensively for medicinal purposes, is sold at an average price of sixty-five francs per 100 kilograms. The seed, being triturated, watered, and heated, as described above, yields in the second pressing from eight to ten per cent. of an oil inferior to that first obtained, and is sold at fifty-eight francs per 100 kilograms. This oil is generally used for lubricating machinery.

The residuum is formed into oil cakes, which are used for fertilizing purposes, and are sold at from 9 to 9.50 francs per 100 kilograms.

The cost of transportation to Marseilles is from thirty to thirty-five francs per ton of 1,000 kilograms.

EGYPTIAN COTTON SEED.

This seed is thoroughly triturated and then pressed twice. In the first pressing it is cold, and it yields from ten to twelve per cent. of its weight in oil. This oil is destined for table purposes, and especially for mixing with olive oil, as it is perfectly tasteless; and for this reason many people also avail themselves of it for frying. It is sold at from eighty to ninety francs per 100 kilograms.

The oil—from eight to ten per cent. of the seed in quantity—obtained in the second pressing, after the usual regrinding, watering, and heating, is of very inferior qualtity, and does not bring a higher price than about fifty francs per 100 kilograms. It is out of the question to use this oil for eating purposes (nor can any of the "*huiles à fabrique*," or oils obtained after the seed has been heated, be used for this purpose), and it is accordingly utilized for the manufacture of soap.

The residuum is made into oil cakes, which are sold at ten francs per 100 kilograms, for feeding cattle and for fertilizing purposes.

The charges for the importation of Egyptian cotton seed into Marseilles are very low, not being above ten to eleven francs per ton of 1,000 kilograms.

NIGER.

Niger is first triturated and then pressed cold. The yield is about eighteen per cent. of the weight of the seed, and the oil so obtained is sold at an average price of about sixty-five francs per 100 kilograms, for mixing purposes.

After being reground, watered, and heated as before described a further yield of fourteen per cent. is obtained, the oil which comes away being used for soap making, for which purpose it is sold at fifty francs per 100 kilograms.

The residuum, as in the case of the other seeds, is made into oil cakes, which are sold as fertilizers for about nine and a half francs per 100 kilograms.

PULGHERIA.

After trituration it is heated before being pressed. The first pressing results in a yield of twenty per cent. of oil which is used in the manufacture of soap. After being triturated again and then watered and heated as usual, ten to twelve per cent. more oil is obtained, which is nearly as good as the first and is destined for the same use. The cost of the oil of the first pressing is fifty-three francs and that of the second from fifty-two to fifty-three francs per 100 kilograms.

It will be noticed that when seed is not pressed cold at all but is heated for both the first and second pressings the values of the oils resulting from both these are nearly the same.

The residuum is made into oil cakes, which are used as fertilizer.

COCOANUTS.

Cocoanuts are pressed twice, being heated and triturated before each pressing. The total yield of oil is from sixty-two to sixty-four per cent., and it is sold for soap making at a cost of from forty-five to forty-eight francs per 100 kilograms.

The residuum is made into oil cakes, which are sold as food for cattle at a cost of eleven to thirteen francs per 100 kilograms.

PALM NUTS.

Palm nuts are pressed twice, being triturated and heated for each pressing. The total yield is from thirty-eight to forty-two per cent. of the weight of nuts pressed, and the oil is sold at fifty francs per 100 kilograms, and is used solely in the manufacture of soaps.

The residuum is made into oil cakes of an inferior quality, which are used as food for pigs.

MOWRAH.

This seed is treated with two pressings, and has to be triturated and heated each time before being pressed. The total quantity of oil obtained is from thirty-seven to forty-one per cent. of the weight of seed pressed, and is sold at the rate of fifty-five to sixty francs per 100 kilograms, for the manufacture of stearin.

The residuum is made into oil cakes, which are of a poor quality, and are sold at three to four francs per 100 kilograms, for manure.

OIL FACTORY STATISTICS.

In order to give some idea of the importance of the oil industry here, and the position it occupies relative to the other chief industries of the town, the following table is submitted. It is taken from a report on the commerce of Marseilles, and shows the ten most important industries, as indicated by the number of hands employed. Where possible, the figures of the exportation of the respective goods have been annexed.

Industry.	Exports.	No. of factories.	Hands employed.
Oil mills	36,950,000 kilograms.	45	3,000
Tile factories	81,107,000 pieces.	99	2,500
Brasieries	.....	31	2,000
Sugar refineries	75,000,000 kilograms.	3	1,800
Soap works	105,000,000 "	90	1,500
Tobacco factory	.....	1	1,500
Tanneries	.....	25	1,350
Cooperages	.....	106	1,340
Iron works	.....	2	903
Flour mills	586,000 quintals.	96	800

PROCESS OF MANUFACTURE.

In the system of presses at present in use in Marseilles the following is the process of manufacture for oil:

The seeds are first put in a mill, where they are thoroughly triturated by means of two upright stones or rollers, the object of this process being to allow the oil to be more readily expressed. The seed so crushed is then divided into several flexible sacks or baskets made of esparto grass and horsehair, and called in French "scourtins," and these are placed one under another, with plates of iron between them, in the press. When pressure is applied, the oil forces its way through the baskets and flows down their exterior surface into a receptacle placed below the press for the purpose of receiving it. Often before the pressing is terminated the action of the press has to be stopped, owing to some of the scourtins being pressed more on one side than on the other, so that they have to be readjusted before the operation can be continued. Care, moreover, has to be taken not to exceed a pressure of about 250 kilograms per square centimeter, equal (roughly) to 31¾ cwts. per square inch, as the scourtins will burst if strained to a higher extent. A drawing of the system described above is herewith submitted (Fig. 1).

ESTRAYER'S CYLINDER.

I have alluded at some length to the system of pressing actually in use for the purpose of comparing it with a new system of oil press invented in Marseilles, for which a United States patent has been applied for (Fig. 2).

This invention consists of a cylinder for olive-oil pressing presenting the double advantage of (1) doing away with the "scourtins," or horsehair sacks, which are replaced by screens of the same substance, by means of which the inventor claims that an economy of as much as eighty or ninety per cent may be realized; (2) a yield of oil highly superior to that obtained by all systems of presses employed up to now.

The cylinder above mentioned is fixed to a cast iron frame supported on flanged wheels, by means of which it can be run upon a truck (shown in Fig. 2), and this truck runs on a track before the presses. By this means the cylinder can be run upon

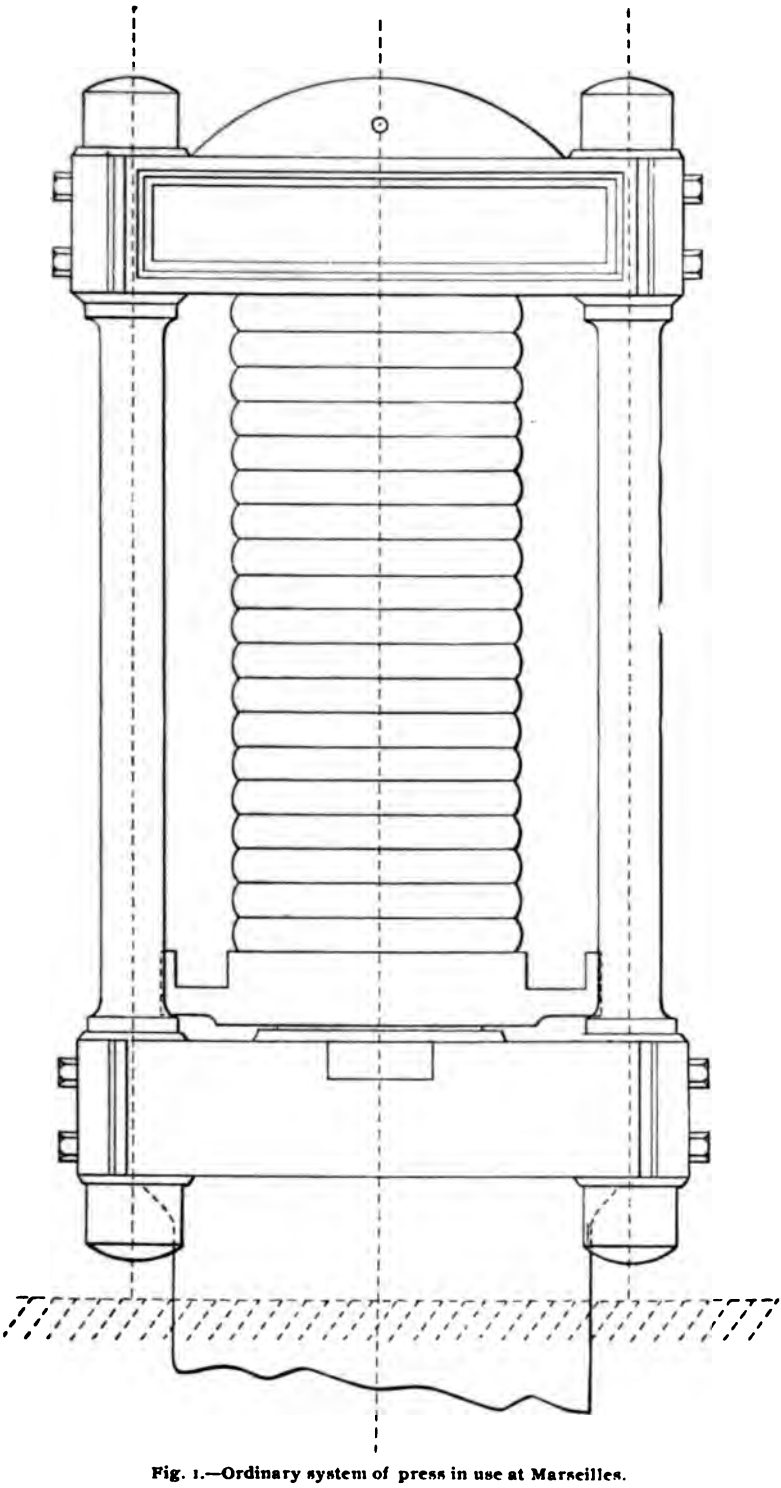


Fig. 1.—Ordinary system of press in use at Marseilles.

the truck, the truck moved till it is opposite any one of the presses, and the cylinder run off under the press for the purpose of pressing.

In cross section the cylinder is octagonal on the inside and circular on the outside (Figs. 4 and 6), and is composed of eight

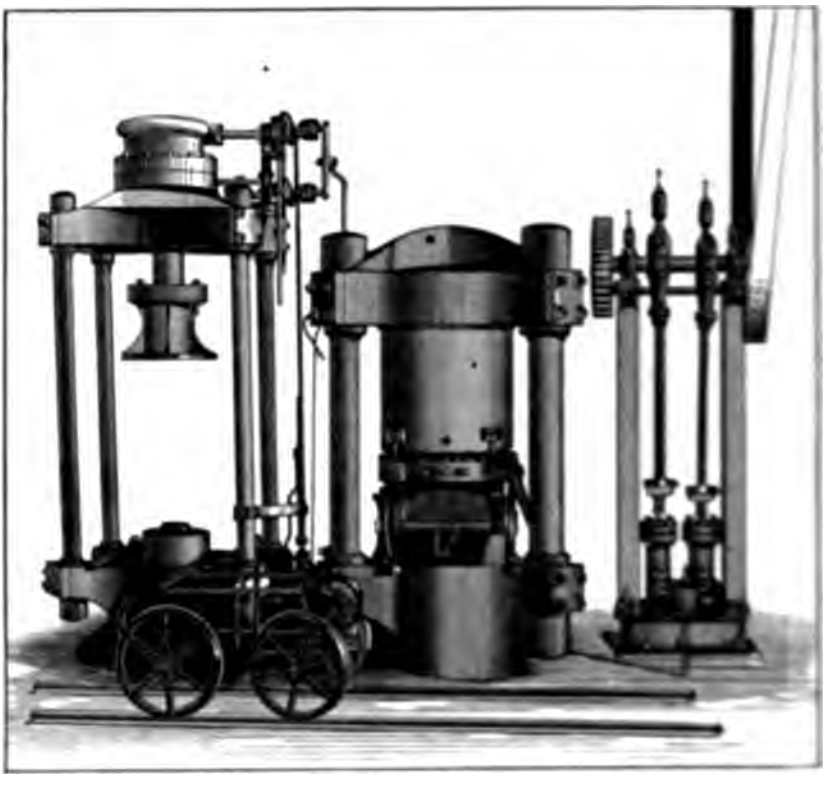


Fig. [illegible] Extractor system of cylinder for oil presses

separate segments of steel which meet with beveled edges [illegible] 3, 4, 5, 6, 7, and 8 in Fig. 4) and on their outer circular surface present a series of inclined planes (*d d d*) in Fig. 6) [illegible] a manner that when the pressure of the grains is terminated an exterior steel case (B B in Fig. 6) which on its interior or concave side is cut in surfaces to correspond with the inclined planes on the exterior of the segments, must be raised vertically

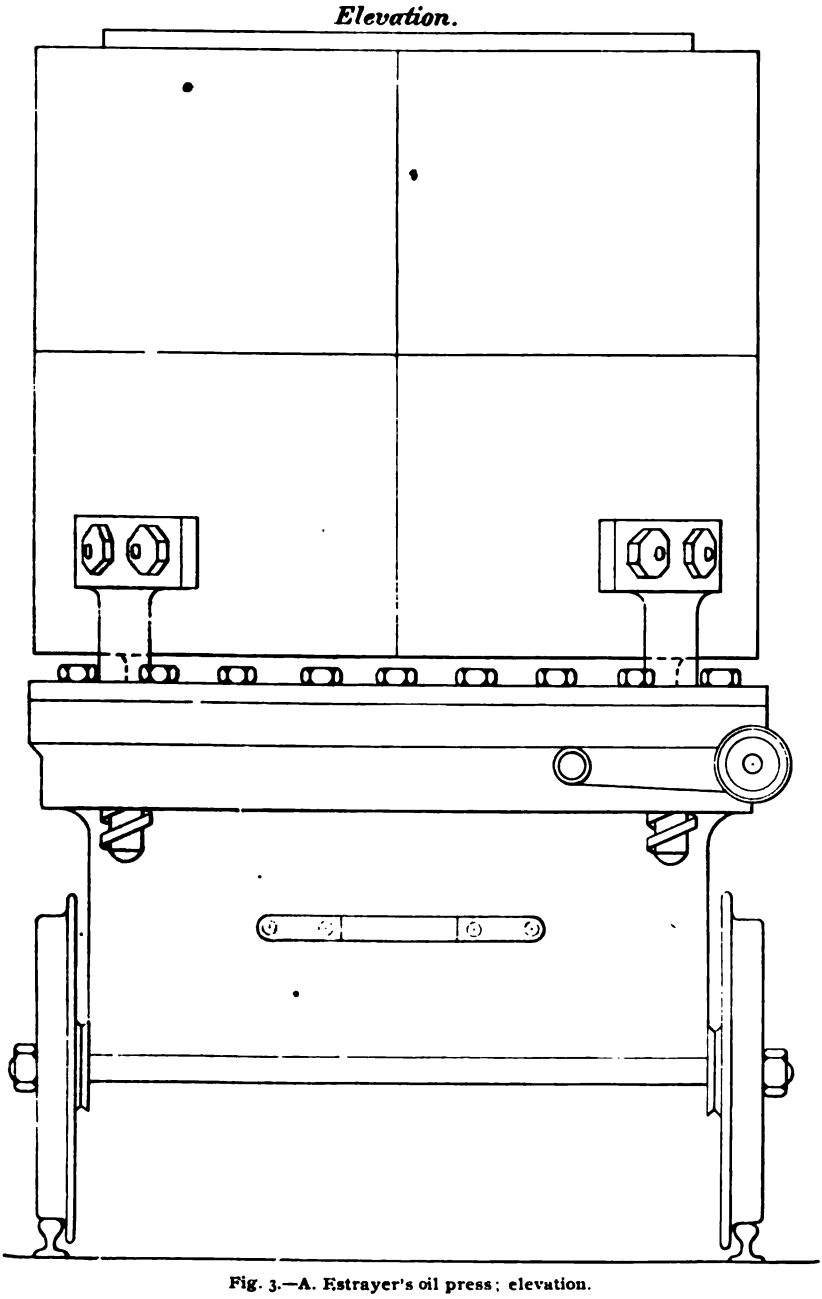
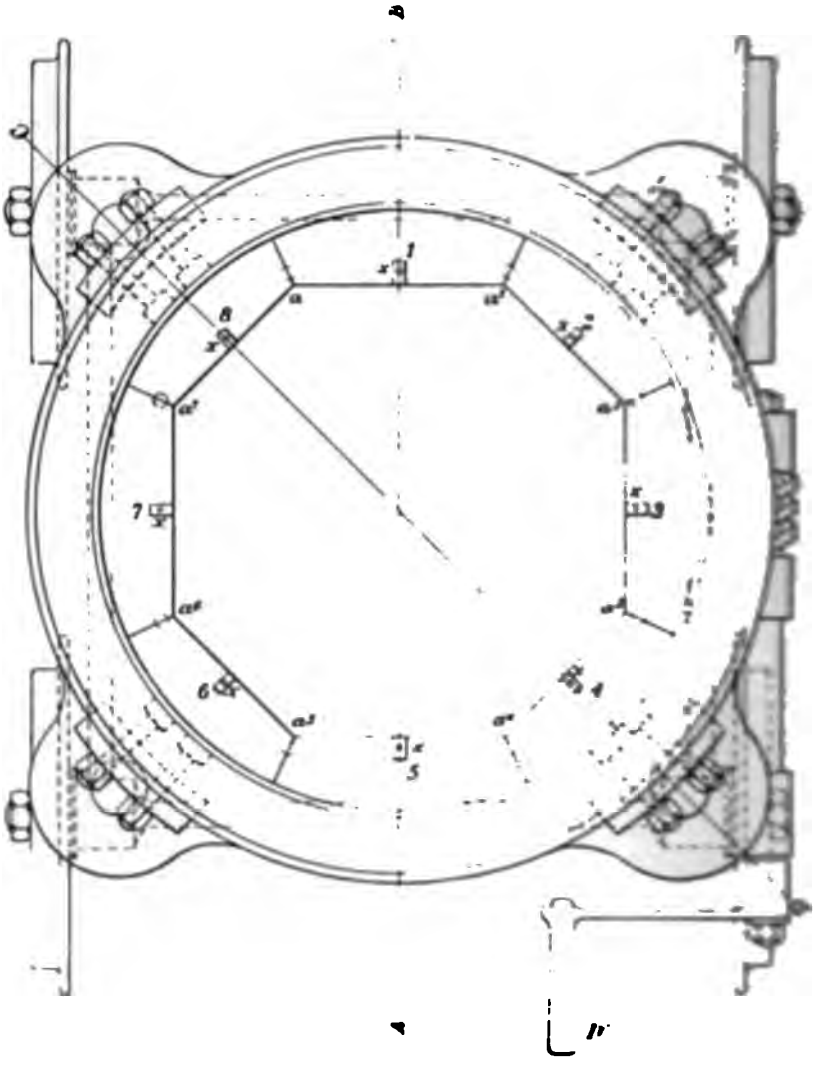


Fig. 3.—A. Estrayer's oil press; elevation.

by means of the cogwheel turned by the handle D (Fig. 4) the handle acting on the cogwheel by means of an endless screw as



shown in Figs. 7 and 8. This cogwheel takes into the six pinions (c Fig. 8) which cause the four rods R to assume a

descend, these rods having a screw turned on their extremity, which is acted on by a female screw on the interior of the pinions. These four rods are bolted to the exterior of the case (Fig. 7)

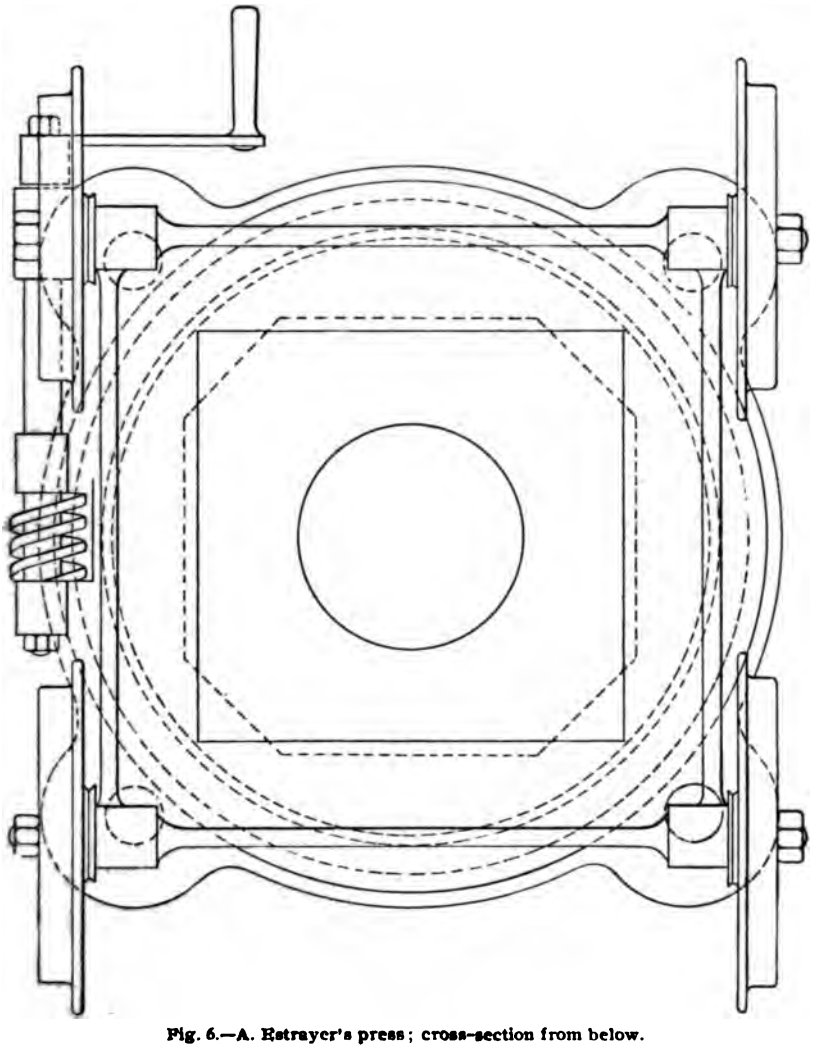
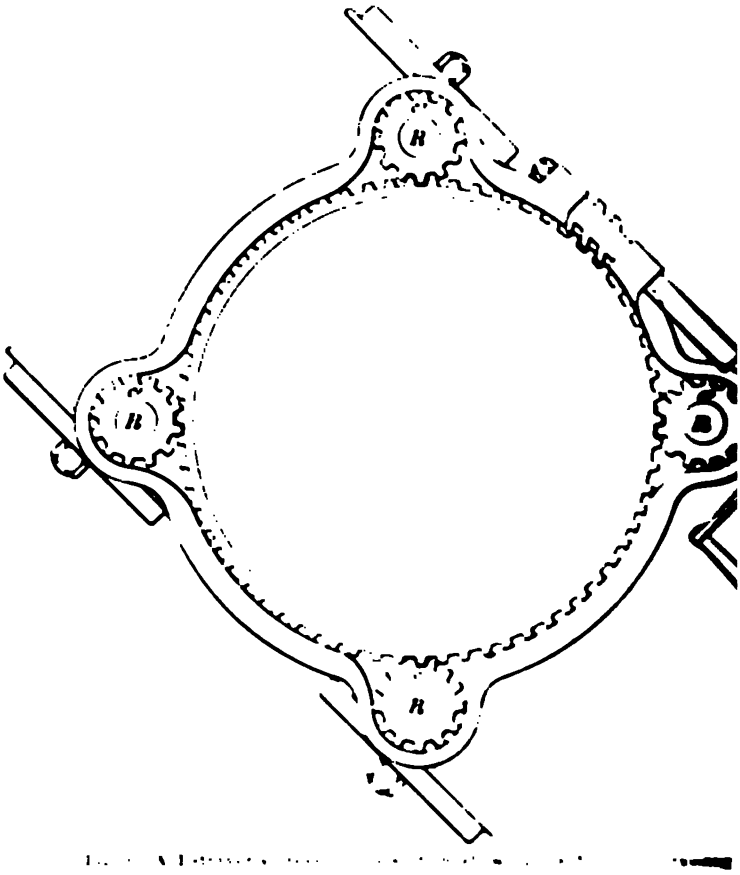


Fig. 6.—A. Estrayer's press; cross-section from below.

and raise it with them till its top is level with that of the cylinder, *i. e.*, the outer case will be raised fifteen millimeters, or about

three fourths of an inch, and it will then be in the pa
indicated by the dotted lines in Fig. 5. When the outer c
in this position the eight segments comprising the cylinder,
no longer in contact with the outer case, will fall slightly
and the plates and hair screens necessary for the lubricati



the oil cake as well as the oil cakes themselves will be
extracted from the top of the cylinder. The chief feature
invention consists of the system of inclined planes running
cularly round the interior of the outer case and acting o
corresponding inclined planes on the exterior of the seg

forming the cylinder for the purpose of tightening them before the oil cakes are pressed and subsequently allowing these segments to be loosened, so that the oil cakes, iron plates, and hair screens may be removed without difficulty or friction. The inventor has reserved to himself the right of raising the outer case for allowing the segments to fall slightly apart, either by hydraulic pistons, or by eccentrics, wedges, or cams.

On each of the beveled faces forming the sides of the segments of the cylinder there is a semicircular groove running from top to bottom of each of the said beveled faces; and the segments being brought close together so that the beveled faces are tight together, as at a, a^1, a^2, a^3, a^4, a^5, a^6, a^7, in Fig. 4, the semicircular grooves come opposite one another and form eight circular conduits running from top to bottom of the cylinder between the eight segments. The ends of these conduits are shown close to the letters a, a^1, a^2, etc., in Fig. 4, referred to above.

The inner face of each of the segments (*i. e.*, the face forming one of the eight sides of the interior of the cylinder) is grooved with parallel channels, which slope downwards from a line drawn down the middle of the inner face of the segment (*b*, in Fig. 5) to its outer edge, where they fall into the conduit between the beveled faces. Over these sloping channels there is placed a series of steel plates (*e*, Fig. 5), these plates being five millimeters wide and five millimeters thick and running from top to bottom of the cylinder, completely lining its interior surface. The plates slide in grooves at the top and bottom of the segments, and the two outer plates in each segment, *i. e.*, those next the beveled edges, are, in addition, held by screws at intervals from top to bottom. The sides of these plates are beveled, and they are placed close side by side all round the interior of the cylinder, with a space between them of not more than one-fourth of a millimeter or thereabouts, as shown in Figs. 5 and 7.

When the apparatus is under pressure the oil squeezed out of the oleaginous matter passes between the steel plates, falls into the sloping grooves behind them, and flows through these into the upright conduits between the beveled faces, which convey it into the receptacle K, this receptacle being provided with a draw-off tap.

In order that the sloping channels and the steel plates in front of them may be cleaned without taking the cylinder to pieces a sliding piece has been provided, which is placed in the center of the grooved plate holding the upper ends of the steel plates in each segment, this sliding piece being held in its place by means of a sunk screw (see x, x, x, in Fig. 4). On removing this sliding piece a hole is disclosed, through which the steel plates may be taken out one after another, thus leaving the sloping channels bare.

The chief features of the invention will be seen on a close inspection of plans 4 and 8 and paragraphs 3 and 5 below as to the manner of working Estrayer's press, and may be summarized as follows: The invention consists of two cylinders, one inside the other, of which the outer acts upon the inner by means of a series of inclined planes, the inner cylinder being composed of eight segments, which either close up tight together or separate slightly, according as pressure is exercised or removed by the position of the outer cylinder.

The resistance of the apparatus is calculated for a pressure of 500 kilograms per square centimeter—say three tons three cwts two quarters per square inch—whereas other presses are unable to stand a pressure of above 350 kilograms per square centimeter or two tons, four cwts., one quarter per square inch without some part of the mechanism being strained.

The manner of working Estrayer's press is as follows:

(1) The working of the cage is extremely simple. It is placed on a truck running on a rail track before the presses and the cylinder itself runs on rails on the truck, these latter rails being at right angles to those on which the truck runs, thus enabling the cylinder to be brought on the truck before any one of the presses and run off the track under the press.

(2) The first precaution to be observed is to see that the outer case inclosing the cylinder is as low as possible and that the eight segments forming the cylinder are in thorough and close contact.

(3) The cylinder is next brought under the preparatory press which is costructed for the purpose and is provided with two pistons, one below acting upwards and one above acting downwards. (The preparatory press is shown at the left hand margin

of Fig. 2, behind the truck). The first or lower piston is designed to discharge the cylinder, *i. e.*, to force the oil cakes up out of it; the second or upper piston serves to ram down the matter to be pressed, in order to make room for more layers of matter by subjecting it to a pressure of 100 kilograms to the square centimeter—say 1,422 pounds to the square inch—before the cylinder is placed under the extracting press, where the pressure exerted is 500 kilograms to the square centimeter—say three tons, three cwts., two quarters (slightly under) per square inch.

(4) The loading or filling is effected in the following manner: The lower piston is raised to within fifteen or twenty centimeters (seven or eight inches) of the top of the cylinder; a hair screen is placed on the piston (the screen having the same surface as the piston head), and the quantity of seed or matter necessary for making one oil cake is poured on the screen, this quantity being regulated by a measuring drawer, which forms part of the preparatory press; on the top of the matter a second hair screen is placed, and above the screen a plate of laminated iron five millimeters (0.197 inch) thick and of the same diameter as the cylinder; on the top of this plate another hair screen is placed, another equal quantity of matter is poured upon it, and so on, repeating the operations already described till the cylinder is full of matter to be pressed, lying between plates of iron having on either side of them hair screens. As the loading proceeds the piston is lowered till the cylinder is full, when the upper piston is lowered to ram down the matter already placed. The piston is then raised and the space obtained by the ramming of the matter is filled up with new layers, and this is repeated till the cylinder is perfectly full. The number of layers will be about twenty to twenty-five, and their total weight eighty to 100 kilograms (one cwt. two quarters to two cwts.).

(5) The loading being finished, the cylinder is run upon the truck to be placed under the extracting press for the high pressure to be exerted in order that the oil may be forced out. This pressing terminated, *i. e.*, thirty to thirty-five minutes later, the cylinder is run under the preparatory press again and in the same position that it occupied during the loading, care being taken to raise the outer case, in order to loosen the eight segments

composing the cylinder before commencing to unload and give the necessary freedom for the extraction of the oil cakes. The lower piston is then raised, and the oil cakes are taken off as they appear above the top of the cylinder. When the last is taken off, the outer case is lowered to tighten up the segments and the loading is recommenced as in 4.

(6) The operations of loading and unloading take about eight or ten minutes, so one preparatory press may serve three or four extracting presses.

The construction of the cylinder is extremely simple. The normal working pressure is 500 kilograms per square centimeter —say 3 tons 3 cwts. 2 quarters to the square inch. An intense movement allows of the cylinder being enlarged in diameter and the movement by which this is effected is very simple. The diameter being enlarged, the oil cakes are no longer in close contact with the sides of the cylinder, and they can therefore be removed without effort. This is a very palpable advantage over all other systems of oil presses, because in their case a pressure of from forty to fifty kilograms per square centimeter say 569 to 711 pounds per square inch—and often more is required in order to force out the oil cake which causes a great delay in the discharging of the press and is also extremely injurious to the apparatus on account of the friction which causes an enormous amount of wear and tear and frequent breakages of the parts destined for the passage of the oil, or else an obstruction of them so great that the oil can only flow away with the greatest difficulty. With Estraver's system it is claimed that all these difficulties are abolished and the apparatus can be discharged and reloaded in seven or eight minutes.

Seeds, etc., such as sesame, peanuts, poppy, Niger etc. can be pressed without any previous trituration in one pressing, which permits of oil of a perceptibly finer quality being obtained.

The yield in the first pressing of Indian sesame is about [illegible] per cent., whereas the best manufactories at Marseilles [illegible] obtain a yield of about thirty per cent. There is a gain therefore of ten per cent. of oil, which at a cost of twenty five francs per [illegible] kilograms, shows a gain of 2 50 francs for every [illegible] kilograms of seed pressed. Besides this there is the economy of [illegible]

the doing away with the hair sacks, the increased value of the oil, and a considerable saving in the amount of labor employed.

For the manufacture of cotton oil the seed must be slightly crushed before pressing, but not so much as with the presses employed in America. The oil will be of better quality. Experiments have been made with Egyptian cotton seed, and one pressing afforded a yield of from 17.5 to 18 kilograms per 100 kilograms of seed, when other presses gave only 13 to 13.5 kilograms. In practice it will be unnecessary to press the seed twice over, for the power of the press and cylinder is such that the same amount can be obtained with one pressing, by leaving the seed in the press a few minutes longer, as the ordinary presses will afford in two pressings, in the first pressing the seed being cold and in the second heated; and, moreover, all the oil obtained with Estrayer's press will be of the first quality, whereas that yielded by seeds after they have been heated (known as "*huile à fabrique*") can only be employed for industrial purposes, and is unfit for table consumption.

Although the cylinder has been constructed for the manufacture of seed oils, it will render equally good service in the manufacture of olive oil, the yield and quality of which will be highly superior to those of oil produced by existing systems.

A factory with twenty presses can press from 50,000 to 60,000 kilograms of seed if the seed be pressed once only, or from 25,000 to 30,000 kilograms if it be subjected to two pressings, with cotton seed.

COMPARATIVE RESULTS.

With the presses in use at Marseilles, seeds from which fine oils are extracted have to be subjected to three pressings, in the first two of which the seed is cold and in the third heated. The yield for 100 kilograms of white Bombay sesame is as follows:

Description.	Yield.	Price per kilogram.	Value.
Oil:	Kilograms.	Centimes.	Francs.
First pressing (cold)	30	75	22.50
Second pressing (cold)	8	62	4.96
Third pressing (heated)	8	50	4.00
Oil cake	54	12½	6.75
Total	100	.....	38.21

The same amount of the same seed is subjected in Estrayer's press to two pressings, in the first of which the seed is pressed whole and cold, and in the second triturated and heated. The yield is as follows:

Description	Yield	Price per kilogram	Value
Oil	Kilograms	Centimes	Francs
First pressing (whole and cold)	[illegible]	[illegible]	[illegible]
Second pressing (triturated and heated)	[illegible]	[illegible]	[illegible]
Oil cake	[illegible]	[illegible]	[illegible]
Total	[illegible]		[illegible]

With 100 kilograms of Egyptian cotton seed the result obtained with the ordinary presses is as follows:

Description	Yield	Price per kilogram	Value
Oil	Kilograms	Centimes	Francs
First pressing (cold and triturated)	[illegible]	[illegible]	[illegible]
Second pressing (hot and triturated again)	[illegible]	[illegible]	[illegible]
Oil cake	[illegible]	[illegible]	[illegible]
Total	[illegible]	[illegible]	[illegible]

The same quantity of Egyptian cotton seed treated with A. Estrayer's system results as follows

Description	Yield	Price per kilogram	Value
	Kilograms	Centimes	Francs
Oil, sole pressing (cold and slightly triturated)	[illegible]	[illegible]	[illegible]
Oil cakes	[illegible]	[illegible]	[illegible]
Total	[illegible]	[illegible]	[illegible]

An oil manufactory containing thirty presses of the type commonly used in Marseilles (Fig. 1) can treat 22,000 kilograms of seed per day of twenty-four hours, the seed being pressed twice, while the same number of Estrayer's presses will treat from 30,000 to 33,000 kilograms of seed pressed twice, or 55,000 to 60,000 kilograms pressed once.

The cost of Estrayer's cylinder with press, is 6,000 francs or $1,158.

A METHOD FOR DETECTING CHLORIN, BROMIN, AND IODIN IN THE SAME MIXTURE.

By Lyman F. Kebler.

As an introduction to this paper it will perhaps be expedient to give first a resumé of the methods previously used for the same purpose. Among these methods there appears to be none that can be executed in a comparatively short time.

Anthony Guyard* detects and estimates the iodids by acidulating the solution with sulfuric acid, then adding a mixture of acid sodium sulfite and copper sulfate. This precipitates the iodin as cuprous iodid. The entire mixture is filtered, the filtrate boiled with an excess of sulfuric acid until the sulfur dioxid is completely expelled. The portion remaining is placed in a flask connected with a Peligot's tube containing acid sodium sulfite, sulfurous acid, carbon disulfid, or potassium iodid; an excess of chromic acid or potassium dichromate and sulfuric acid is added to the flask and the mixture boiled until the bromin is all expelled and absorbed in the Peligot tube. After reducing the excess of chromic acid the chlorin is detected in the usual manner.

G. Vortman† bases his method on the following reactions: The peroxids of lead and manganese, in an acetic acid solution, completely decompose the iodids; the bromids are decomposed only by peroxid of lead in an acetic acid solution, while the chlorids remain intact.

Paul Julius‡ describes a method which is further examined the following year, by F. Maxwell Lyte.§ These investigators take advantage of the solubility of the double cyanids.

E. Hart‖ gives the following method for detecting the halogens: The solution, contained in a flask connected with a bulb tube condenser, is treated with a solution of ferric sulfate; this liberates the iodin. The iodin is distilled into the bulb tube containing starch solution. After the iodin is all evolved a few drops of chloroform are placed in the bulb tube and a small

* 1879, Bull. soc. chem., 31, 301; Ztschr. anal. Chem., 18, 478.

† 1880, Ber., 3, 525; Abstr., Am. Chem. J., 2, 199.

‡ 1883, Chem. News, 48, 284.

§ 1884, Chem. News, 49, 3.

‖ 1884, Am. Chem. J., 6, 346.

fragment of potassium permanganate is added to the portion remaining in the flask and the contents heated to boiling. If bromin is present the chloroform will assume a reddish hue. In case bromin is present more potassium permanganate and ferric sulfate solution are added, distillation continued until all of the bromin is evolved. The excess of potassium permanganate is reduced with ethyl alcohol and the remaining solution tested for chlorin as usual.

M. Dechan also gives* an ingenious method. He treats a solution containing the halogens with potassium dichromate (forty parts in 100 parts of water), boils the mixture in a flask connected with a condenser and receives the distillate in a test tube containing a few drops of carbon disulfid. If iodin is detected the distillation is continued until no more iodin comes over. Then for every 100 cc. of potassium dichromate solution used he adds eight cc. of fifty per cent. sulfuric acid, boils again in the same flask, testing the distillate for bromin as for iodin above. After the bromin is all expelled the excess of chromic acid is reduced and the solution tested for chlorin in the usual way. Dechan has also devised† an apparatus to be used with his method.

L. L. de Koninck‡ presents a method for detecting chlorids in presence of bromids. The haloids are precipitated with silver nitrate, the silver chlorid is removed from the silver salts and the silver bromid by boiling them with a solution of ammonium carbonate.

I have modified this method as follows. After the silver chlorid has been removed the silver bromid is removed with ammonia. By this means we have a complete separation but there appears to be some difficulty in separating the silver chlorid from the other silver salts by means of ammonium carbonate.

J. E. Whitfield§ gives a method for estimating the above elements by means of electrolysis. This method can also be employed to detect them qualitatively.

[illegible]

In all* of the above methods, as well as in my own, it is necessary to employ the soluble halogen salts. If they are present as silver salts, the material is fused with sodium bicarbonate and the mass extracted with water; if present as chlorates, bromates, and iodates, the substance is fused on charcoal with sodium bicarbonate and the mass treated as above.

The following method of my own has been in successful use for five years past and has given perfectly satisfactory results in the hands of ordinary qualitative students.

In order to test the accuracy of the method many mixtures were prepared and analyzed by the author. The mixtures contained from one to ten per cent. in the solid state, or from one-tenth to one per cent. each in solution of chlorids, bromids, and iodids, and in no case was there any difficulty experienced in detecting the individual elements. The only precaution necessary is to watch carefully when the iodin and bromin are evolved. This can easily be determined by means of the carbon disulfid test.

The method is as follows: To a solution supposed to contain chlorids, bromids, and iodids, add a few drops of nitric acid, specific gravity 1.42; warm gently and the iodin will be liberated if an iodid is present; cool the solution and determine the presence or absence of free iodin by adding a few drops of carbon disulfid which assumes a purple color in presence of free iodin. If the carbon disulfid does not assume a purple hue, but a yellowish-brown, a bromid is present. In case iodin is present add more nitric acid, heat a few moments, cool the solution, and test for the presence or absence of iodin as before with carbon disulfid. If the iodin has all been evolved the carbon disulfid will assume a yellowish-brown color in presence of a bromid. In case bromin is revealed add more nitric acid and boil the solution until the bromin is all evolved, which is generally indicated by a nearly colorless solution and is definitely decided by means of the carbon disulfid. After the bromin has all been expelled add a few drops of silver nitrate to the solution; the formation of a white precipitate soluble in an excess of ammonia and insoluble in nitric acid indicates a chlorid.

* Possibly excepting L. L. de Koninck's, but that works better with freshly prepared silver salts.

There are several ways of applying the carbon disulfid test. For the results in this paper the tests were applied as follows. In each case a few drops of the hot solution were poured into a small test-tube, cooled, the carbon disulfid added and slightly agitated.

NOTE ON THE PRECIPITATION OF PHOSPHORUS FROM SOLUTIONS OF IRON AND STEEL.*

By Robt. Hamilton, F. I. C.

The rapid and correct estimation of phosphorus in iron and steel is of such technical interest and importance that I imagine any information concerning it will be welcome to many members of our Society.

Of the many methods proposed for this estimation that chiefly employed is one form or another of the method depending on the precipitation of the phosphorus as ammonium phosphomolybdate, often spoken of as "yellow precipitate."

It was known for many years that unless certain precautions were taken in dissolving the sample, there was a liability to obtain a solution from which the ammonium molybdate solution would not precipitate the whole of the phosphorus.

In 1877, And. A. Blair and Finkiner independently attributed this interference to the presence of carbonaceous matter in the solution, derived from the action of acids on the combined carbon of the metal, and they directed that the operation of solution should be conducted in such a manner as to destroy these carbonaceous compounds. This was practically effected by evaporating the acid solution to dryness and roasting the residue.

Adolf. Tamm (*Chem. News*, 1884) accentuated the same view.

There are methods founded on the above mentioned observations which leave nothing to be desired in point of accuracy, but the evaporation to dryness with subsequent roasting and re-solution consumes much time, besides the minor inconveniences caused by large amounts of acid fumes.

Having a considerable amount of work to get through, I naturally neglected no opportunity of trying processes which promised to save time, and I may preface my further remarks

* See Chem. Ind., 15, 5.

by saying that my object was to obtain a rapid process for the correct estimation of phosphorus in hematite pig iron.

In 1888, P. W. Shimer suggested that the incomplete precipitation of phosphorus was due to incomplete oxidation of the phosphorus, and proposed to render all the phosphorus precipitable by oxidizing the solution with potassium permanganate, etc.

The experiments recorded in this paper would appear to show that this view has much to commend it.

For the estimation of the phosphorus, Shimer used the filtrate from the determination of silicon by the nitric and sulfuric acids method. It was tried at the time with unsatisfactory results, though I now believe that, with a little practice, good results could be obtained; but the method presented no advantages over the one I then used, and it was not followed up.

In 1889, Dr. Drown supported Shimer's idea and introduced an important improvement conducing to rapidity, namely, the solution of the metal in *dilute* nitric acid, thus retaining practically the whole of the silica in solution, but in this case the yellow precipitate should not be weighed, but, if large enough, should be converted into magnesium pyrophosphate; or, if too small for that, may be reduced with zinc and the solution titrated with standard permanganate. This method was carried out at the time exactly as described (*Chem. News*, July, 1889) and unsatisfactory results obtained.

At intervals there continued to appear in the journals slight modifications of the foregoing methods, and the advantages offered were so tempting that I determined to perform a few experiments to find out whether the idea was a correct one or not. Though the process was wanted ultimately for hematite iron, yet the proportion of phosphorus in that iron is so small that experimental error forms a larger factor and renders the results less decisive than if operating with an iron containing more phosphorus; besides it is desirable to weigh the phosphorus as magnesium pyrophosphate whenever possible, so I determined to work with phosphoric iron.

First, to see what effect the presence of the carbonaceous matter had, a sample of hematite white pig-iron was selected, low in phosphorus and high in combined carbon.

A full analysis was not made, but the following figures will give a fair idea of its composition: phosphorus, 0.037 per cent; silicon, 0.71; sulfur, 0.26; graphite, a trace, and combined carbon fully equal to that of a pig to be mentioned further on which had 2½ per cent. of combined carbon.

The general details of the method followed are much the same in each case, and I shall describe the first experiment fully and only detail the *differences* in those following.

Experiment No. 1.—Twenty-five grains sample plus [illegible] measured grains of nitric acid (1 : 2), evaporated till a good deal of iron salt dried, taken up with hydrochloric acid, evaporated to small bulk, diluted, filtered, evaporated till skin just began to form, added excess of ammonia, then a slight excess of nitric acid, then molybdate solution, gave yellow precipitate, equal to [illegible] per cent. phosphorus, equal to eighty-one per cent. of the phosphorus present.

A solution of phosphoric acid was prepared of such strength that 100 measured grains contained about 0.25 grain of phosphorus, so that 100 grains of the phosphoric acid solution added to twenty-five grains of the pig iron came to about the same thing as working with a sample of iron containing one per cent. of phosphorus.

Experiment No. 2.—Twenty-five grains iron plus [illegible] grains nitric acid (1 : 2), heated till all dissolved, added [illegible] grains phosphoric acid solution, then proceeded with as before, gave magnesium pyrophosphate equal to all the phosphorus added as phosphoric acid, plus that derived from the sample of iron.

Experiment No. 3.—Twenty-five grains iron plus nitric acid and phosphoric acid as last, evaporated till the solution would just run, but no iron salt dried, then exactly as before, gave the whole of the phosphorus present.

Experiment No. 4.—A repetition of the last gave the same result.

Experiment No. 5.—Twenty-five grains iron plus nitric acid and phosphoric acid as before, but evaporated only to half bulk and without filtering proceeded with as before, gave the whole of the phosphorus present. The filtrate from the yellow precipitate was dark sherry colored, and the ammonium magnesium phosphate was mahogany colored.

Experiment No. 6.—To test if the action of solution had any effect on the phosphoric acid, 100 grains of the phosphoric acid solution was measured out, twenty-five grains iron added, then nitric acid, evaporated to half bulk, and proceeded with as last, gave the whole of the phosphorus present; colors of solutions and precipitates same as last.

These experiments seemed to prove that the presence of carbonaceous matter in solution did *not* prevent the precipitation of phosphorus which existed as phosphoric anhydrid in combination.

The next step was to find out if the phosphorus in iron could be rendered completely precipitable by oxidation while in solution. For this purpose the following experiments were made with a sample of white pig iron, made when a furnace was being blown in, of the following unusual composition:

WHITE PIG IRON (PHOSPHORIC).

	Per Cent.
Graphite	0.67
Combined carbon	2.54
Total carbon	3.21
Silicon	0.39
Phosphorus	1.36
Sulfur	0.20
Manganese	0.69
	5.85
Iron (by difference)	94.15
	100.00

For the remainder of this paper, when iron is mentioned, this white iron with 1.36 per cent. of phosphorus is meant.

Experiment No. 7.—Twenty-five grains iron plus 500 grains nitric acid (1 : 2), evaporated to half bulk, added excess of ammonia, slight excess of nitric acid and molybdate solution. Phosphorus finally weighed as magnesium pyrophosphate equalled seventy per cent. of the phosphorus present. The filtrates were all tested, but this one was especially worked with, but no more yellow precipitate was obtained.

At *Experiment No. 8*, I began to try the effect of oxidizing agents. Twenty-five grains iron plus 500 grains nitric acid (1 : 2), boiled, plus three additions of 100 grains each of ten

vol. hydrogen peroxid, boiling between each addition, evaporated to half bulk, and proceeded with as before, gave magnesium pyrophosphate equal to ninety-five per cent. of the phosphorus present.

The hydrogen peroxid destroyed the combined carbon while the solution became clear and the precipitates were pure yellow and white respectively.

It is hardly necessary to mention that the hydrogen peroxid and other chemicals used were tested for phosphorus.

Experiment No. 9.—Twenty-five grains iron treated as last, the only difference being that five additions of hydrogen peroxid of 100 grains each were made, instead of three as before, gave magnesium pyrophosphate equal to 99.3 per cent. of the phosphorus present.

To avoid the boiling between each addition of hydrogen peroxid, the following experiment (*No. 10*) was tried. Twenty-five grains iron plus nitric acid, boiled, cooled, added 300 grains of a fresh solution of twenty vol. hydrogen peroxid, allowed to stand for twenty minutes, then heated very slowly and boiled down to half bulk, then as before, gave magnesium pyrophosphate equal to only eighty-five per cent. of the phosphorus present.

Small additions of hydrogen peroxid, boiling after each addition, seemed to render all the phosphorus precipitable, but the cooling between each addition was a loss of time, besides there was nothing to show when enough of the oxidizing agent had been added.

In Shimer's paper it is directed to add the permanganate solution (the oxidizing agent he used) till a precipitate of hydrated manganese peroxid comes down; this seemed a useful visible reaction, and it was resolved to test it.

For *Experiment No. 11*, twenty-five grains iron were taken plus 500 grains nitric acid (1.42), boiled, and a solution of permanganate added till the desired precipitate came down; the solution cooled, twenty drops hydrogen peroxid added, boiled, neutralized with ammonia, boiled again with a little permanganate till a precipitate came down, which was removed again with hydrogen peroxid, the solution evaporated to half bulk and proceeded with as before, gave magnesium pyrophosphate equal to 99.7 per cent. of the phosphorus present.

The use of hydrogen peroxid for deoxidizing the manganese peroxid precipitate is both elegant and effective, but as the solution requires to be cooled to about 130° F. before adding it, there is a slight loss of time.

Shimer dissolved the manganese peroxid precipitate in hydrochloric acid, and Drown removed it with an organic acid or with sugar. When trying Drown's method, I had used tartaric acid, but had not got satisfactory results with it, and Jones (*Chem. News*, 1890) found the same thing, and proposed the use of ferrous sulfate.

Five experiments were performed very much the same as the most successful of the experiments already mentioned, oxidizing the solution with permanganate, and removing the manganese peroxid precipitate with ferrous sulfate; without going into details, I may say that the lowest result equalled 94.1 per cent., and the highest, 96.3 per cent. of the phosphorus present.

In each of the foregoing experiments (excepting two of the five with ferrous sulfate) the yellow precipitate was allowed to settle for hours, usually over night, but to save time I now tried the effect of shaking for five minutes as proposed by Emmerton, and filtering straight off.

Experiment No. 12.—Twenty-five grains iron plus 700 grains nitric acid (1 : 135, being the strength recommended by Drown for keeping the silica in solution), oxidized twice with permanganate, removing the precipitate with hydrogen peroxid and neutralizing with ammonia between the two oxidations, the flask stoppered and shaken vigorously for five minutes, cooled and filtered, gave magnesium pyrophosphate equal to 96.3 per cent. of the phosphorus present.

Experiment No. 13.—The above experiment repeated, gave 100 per cent. of the phosphorus present.

Even a single oxidation gave very fair results, as follow:—

Experiment No. 14.—Twenty-five grains iron plus 700 grains nitric acid (1 : 135), oxidized with permanganate and hydrogen peroxid, neutralized with ammonia, molybdate solution added, shaken for five minutes, cooled and filtered, gave magnesium pyrophosphate equal to 96.3 per cent. of the phosphorus present.

Experiment No. 15 is exactly similar to the last, that is, the

solution was only oxidized once, but the yellow precipitate was allowed to stand for one and a half hours before being filtered off, and the magnesium pyrophosphate obtained was equal to 100 per cent. of the phosphorus present.

The magnesium pyrophosphate precipitates from five experiments in which dilute nitric acid had been employed, were added together and tested for silica by evaporating to dryness with hydrochloric acid, etc.; the insoluble matter weighed only [illegible] grain, which may fairly be allowed to have been derived from the filter ashes, and evidently the precipitates have been free from silica.

At this point I may refer to an experiment of some interest only completed this morning.

Experiment No. 10.—In this experiment I took twenty five grains of the white phosphoric iron, added [illegible] grains nitric acid (1 : 2) and boiled, neutralized with ammonia, and precipitated with molybdate solution. The flask stood a few hours the precipitate had settled thoroughly and left a clear liquid which was decanted through a filter and the precipitate washed once.

To the clear filtrate I added permanganate solution and placed it on the water bath, in a short time the liquid became turbid and deposited yellow precipitate. After standing about [illegible] I added excess of hydrogen peroxid and allowed it to settle [illegible] night; when filtered and weighed this morning the yellow precipitate equalled thirty three per cent. of the phosphorus [illegible] pig iron. Referring to experiment No. [illegible] it will be [illegible] that it is so far much the same as No. 10 only the original nitric acid solution was evaporated further and gave seventy per cent. of the phosphorus present so it may be considered that the [illegible] three per cent. found in the filtrate of experiment No. [illegible] was the whole of the phosphorus in that filtrate.

Experiment No. [illegible]—One other experiment may be [illegible] which goes to support the oxidation theory.

In the *Chemical News* of March [illegible] there was an abstract of a paper by Clerc recommending the employment of [illegible] and hydrochloric acid for the estimation of silicon in iron.

Using the white phosphoric pig iron before mentioned and following exactly the directions given only fifty per cent. of the

silicon was obtained, but the filtrate yielded on proper treatment, without either evaporation to dryness or further oxidation, magnesium pyrophosphate equal to 99.7 per cent. of the phosphorus present.

I think it may be fairly assumed that the two sets of experiments quoted prove to satisfaction (1) that the carbonaceous matter in a solution of iron does not prevent the complete precipitation of properly oxidized phosphorus as ammonium phosphomolybdate; (2) that the reason of the incomplete precipitation of phosphorus from a nitric acid solution of iron, which has not been evaporated to dryness and roasted, is that the phosphorus has not all been properly oxidized; and (3) that in such solutions all the phosphorus can be completely oxidized and rendered precipitable, in the wet way, by means of certain oxidizing agents.

In conclusion, I cannot claim much originality for any of the experiments quoted, but I think they put this point in a clearer light than it has been, and, at any rate, they have served their purpose, inasmuch as there has been founded upon them a rapid and accurate method for the estimation of phosphorus in hematite pig iron.

A NEW BLEACHING POWDER PROCESS.

The following description of Mr. Ludwig Mond's new bleaching powder process is taken from the *London Times*. After a digest of the various operations employed in the manufacture of ammonia-soda, the *Times* says:—

Instead of boiling his ammonium chlorid with lime, Mr. Mond freezes it by means of an ammonia refrigerating apparatus, which by passing the gas through an endless cycle of condensations and expansions produces any required amount of cold. Treated in this way the ammonium chlorid crystallizes out of the solution. It is dried and subjected to the opposite extreme of temperature. Somewhere about a red heat it sublimes and probably suffers temporary decomposition, the hydrochloric acid and the ammonia existing in the vapor as separate and uncombined gases. The vapor is passed over magnesium oxid mechanically arranged so as to present the largest possible surface. Then comes the

characteristic reaction of the new chlorin recovery process. The magnesium oxid gives up its oxygen, which combines with hydrogen to form water. In place of the oxygen the magnesium combines with the chlorin of the ammonium chlorid and free ammonia is obtained and collected in the usual way. At this point, therefore, the account stands thus—bicarbonate of soda in the solid form, only needing to be heated to give soda ash; the ammonia used in the process wholly recovered, barring a percentage of waste, in its original gaseous state; and the chlorin wholly fixed as magnesium chlorid. Now the reaction which produced magnesium chlorid is exactly reversed. Hot air is passed over the chlorid as hot chlorin was passed over the oxid, and as the chlorin of the ammonium chlorid drove out the oxygen of the oxid, so now the oxygen of the air drives out the chlorin of the chlorid. The free chlorin is passed over the caustic lime from the kilns after it is slacked with water, producing bleaching powder, and the magnesium oxid is left in its original condition ready to decompose a fresh batch of ammonium chlorid. Thus the chlorin of the original brine is combined with the lime of the original chalk, the soda of the brine is combined with the carbonic acid of the chalk, the ammonia and the magnesium oxid employed in the process have been given back in their original forms, and nothing has disappeared except the coal which has furnished the heat required to effect the transformations.

The Editor of the *Chemical Trade Journal*, from which the above account is taken, comments on it in part as follows:

As we have said before, the process is not so simple as it looks. The waste liquors from the carbonates are not pure water. Suppose them to contain six per cent. of ammonia they will also contain nearly eight per cent. of salt, while of the ammonia itself seventy-five per cent. only is chlorid, the remaining twenty-five per cent. being either a carbonate or chlorid in contact with bicarbonate of soda.

We are not attempting to argue that the recovery is not possible *at a price*, but we are brought face to face with all the difficulties of the muriate of ammonia sublimer, and all who know that business will be only too ready to assert that they are real. Add to these the difficulties that have been encountered in the

"Weldon Magnesia" process, the "Weldon-Pechiney" process, and the "Deacon" process, and we have the "New Departure" in a nutshell.

Backed by enormous resources, there is no doubt that "bleach" may be made by the New Departure for a longer period than would be the case in a smaller concern, but if the revenue is not greater than the expenditure it is only another process of assuring the continuance of remunerative prices for ammonia-soda.

CONCERNING THE NAME OF THE ELEMENT COLUMBIUM.

The following correspondence is self-explanatory. Copies of Prof. Brown's letter were sent to Professors Norton and Clarke and their replies follow.

WASHINGTON AND LEE UNIVERSITY,
Lexington, Va., Nov. 7, 1892.

DR. HART,

DEAR SIR:

In the September number of your JOURNAL, p. 535, Prof. Norton says, concerning the name Columbium "discovered and named by an American chemist." This is no good reason for retaining the name, even were it correct, but it is not. Hatchett, who proposed the name, was an Englishman, according to Prof. J. D. Dana who, in his "System of Mineralogy," 5th Edition, p. 518, says: "No good reason has been given for substituting Niobium for Columbium; and yet most English chemists, as well as European, have thus far followed Rose in rejecting the name given by the English discoverer. *The rule of priority demands recognition.*"

The last sentence gives the reason for abiding by Columbium.

Kopp, "Geschichte der Chemie," Vol. 4, p. 77, says: "Das Tantal würde zuerst durch den Engländer Hatchett wahrgenommen, * * * von ihnen Columbium genanntes."

Yours truly,

W. G. BROWN.

P. S.—If an American chemist has discovered an element, it was Dr. J. Lawrence Smith, who named one mosandrum.

W. G. B.

CINCINNATI, Nov. 12, 1892.

MY DEAR PROFESSOR HART:

Your favor of the 9th just received. Prof. Brown's criticism is quite correct. The New England origin of the mineral columbite in which the presence of the new element was detected,

led me inadvertently to overlook the fact that Hatchett was an Englishman and made his communication to the English Philosophical Transactions in 1802.

The historical priority of Columbium should, however, scarcely be questioned. In the year following Hatchett's discovery Ekeberg announced the presence of the new metal tantalum in the mineral tantalite. The close similarity of Hatchett's columbic acid and Ekeberg's tantalic acid led Berzelius and others to claim for many years that they were identical, and the name given by Berzelius' compatriot Ekeberg displaced to a great extent that of Hatchett, although the latter was indisputably of earlier date.

In 1844 Rose (and others during the next decade) showed that the acid in tantalite was not homogeneous, but contained from nine to thirty per cent. of what we now term columbic acid, and further that the acid in columbite was rarely pure, but contained usually from thirty to [illegible] per cent. of tantalic acid.

Rose unfortunately gave the name Niobium to the element predominating in columbite and present to a less extent in tantalite, and his [illegible] has been largely followed in Europe, in total disregard of the [illegible] custom of respecting the rights of discoverers.

It is certainly of interest to us Americans to see the usage of the historically correct name of the element in question restored, especially since the name is linked so emphatically with the one instance in which a [illegible] from our own land has proved to be the source of a new element.

Very sincerely yours,

T. H. [illegible]

WASHINGTON, D. C., [illegible]

DEAR SIR:

Hatchett, as Brown says, was not American but English. In 1801 he discovered the new metal Columbium in a mineral which was called columbite, and which very probably came from Massachusetts or near there. In 1802 Ekeberg discovered tantalum in tantalite. For some time after it seemed as if tantalum and Columbium might be identical. Later Rose, studying columbite, thought he had found two new elements, which he named niobium and pelopium. The latter was soon abolished, and niobium was found to be identical with the greater part of the new metal found by Hatchett in columbite. The metallic acids from Connecticut columbite are about one third tantalic to two thirds [illegible]. Hatchett's name, therefore, represents the dominant [illegible] mineral, while Rose's Niobium merely stands for a [illegible] had Columbium freed from a small impurity of admixed tantalum. The rule of priority is clear, and the struggle by which Niobium came [illegible] should be discontinued.

Very very truly,

F. W. [illegible]

THE CONSTITUTION OF MAGNETIC OXIDS.

By Stephen H. Emmens.

In the process of nickel manufacture practised by the Emmens Metal Company at Youngwood, Westmoreland Co., Pa. the metal is granulated by pouring it, when molten, into water. This operation usually proceeds quietly and without interruption; but occasionally sharp explosions take place as the metal touches the surface of the water. Investigation into the conditions of these explosions has shown that the phenomenon is always accompanied by a more or less oxidized state of the molten metal; that is to say, the nickel ore has not been completely reduced to metal in the operations preceding that of granulation.

It is also noticed that when no explosions occur, and when the molten metal sinks quietly to the bottom of the granulating vessel, bubbles of gas rise to the surface of the water and burn there with a blue flame.

Inasmuch, then, as the fully-reduced metal appears to decompose water, and as the partially-reduced metal causes an explosion when coming into contact with water, it would seem that, in the latter case, the presumably homogeneous mass of molten metal consists partly of molecules of free nickel which liberate hydrogen from the water, and partly of molecules of nickel oxid which supply oxygen to at once combine explosively with the hydrogen.

This explanation, namely, that an oxid of nickel probably exists in which the metal is partly metallic and partly oxidized, suggests an analogous explanation of an analogous phenomenon, *i. e.*, the magnetic character of certain oxids.

Chemists have hitherto been, for the most part, agreed in considering the magnetic oxid of iron, Fe_3O_4, as being, to quote Mendeléeff (*Principles of Chemistry*, translated by Kamensky and Greenaway), "composed of ferrous and ferric oxids." Indeed, Mendeléeff specifically speaks of "the so-called magnetic oxid, containing atomic quantities of the suboxid and oxid, viz., $FeO,Fe_2O_3 = Fe_3O_4$." And the new edition of Watts' *Dictionary* says "Fe_3O_4 may be regarded as FeO,Fe_2O_3"; while the old

edition (Second Supplement) gives the following graphic formula for Fe_3O_4:

$$\begin{array}{ll} Fe = O & \\ \quad\quad\;\; O & \\ \quad\quad\;\; O & \quad Fe \\ Fe = O & \end{array}$$

in which ferrous (bivalent) iron is represented as forming an unsaturated compound, FeO_4, which is united with an unsaturated compound, Fe_2O_4, of ferric (in this case quadrivalent) iron. Drechsel, on the other hand (*Introduction to the Study of Chemical Reactions*, translated by Merrill), admits Fe_3O_4, or rather Fe_6O_8, to a place among the true iron oxids, and pictures its constitution as follows:

$$\begin{array}{lll} Fe^{iv} & O'' & \\ & O & \\ & O & (Fe^{iv} = Fe^{iv}) \\ Fe^{iv} & O & \end{array} \qquad \begin{array}{ll} O'' & Fe^{v} \\ O & \\ O & \\ O & Fe^{v} \end{array}$$

contending that iron is quadrivalent only and not at any time either bivalent or trivalent.

None of these views throw any light upon the most remarkable property of Fe_3O_4; that is to say, they show no reason why it should be much more magnetic than its fellow oxids and especially than the protoxid, FeO, which contains a larger percentage of the metal. The question, therefore, of the true molecular constitution of magnetic iron oxid may be regarded as being still an open one; unless, indeed, there be any considerations of paramount importance already advanced sufficiently compelling the recognition of $FeO.Fe_2O_3$. If we search for such reasons, we shall find them to be two in number, viz.

1. The argument from isomorphism. – Magnetite (Fe_3O_4) is found in nature as a mineral isomorphous with spinel ($MgAl_2O_4$), gahnite ($ZnAl_2O_4$), zeilanite ($FeAl_2O_4$), franklinite ($ZnFe_2O_4$) and chromite ($FeCr_2O_4$). It is assumed that spinel must contain MgO, that gahnite and franklinite must contain ZnO, that zeilanite must contain Al_2O_3, that chromite must contain Cr_2O_3, and that therefore the former three must also contain Fe_2O_3, and the latter two FeO. But if these assumed necessities do not

in point of fact exist, the argument falls to the ground; and as no attempt is made to prove their existence we are justified in treating the argument as of no weight,—a very frequent thing in cases of isomorphism.

2. The argument from solution.—If Fe_3O_4 be dissolved by acids, ferrous and ferric salts are found in solution. This is held as proof that Fe_3O_4 consists of FeO and Fe_2O_3. But if Fe be dissolved by H_2SO_4 and form $FeSO_4$,Aq., no one dreams of declaring that Fe must have contained FeO. Solution certainly implies a degree of molecular disaggregation that admits of rearrangement; and so far from the presumption being in favor of a continuance of pre-existing molecular structure, it is obviously the reverse.

Seeing, then, that no good reason exists for regarding Fe_3O_4 as FeO,Fe_2O_3, it may be well to enquire whether any valid arguments can be advanced *against such a view*.

First, the compound Fe_2O_3 is of a very stable character, and is, with reason, regarded as "saturated." If, then, it be linked to FeO, this can only be by means of some hitherto unknown and unrecognized affinity invented or imagined for the occasion.

Secondly, FeO is of a very unstable character; so much so, indeed, that the ordinary assumption of its being "saturated" appears to have very slender foundation. Its combination with Fe_2O_3 by means of the mysterious affinity above mentioned should not, apparently, interfere with its proneness to oxidation; and the compound FeO,Fe_2O_3 should readily change into $2Fe_2O_3$, whereas, in point of fact, Fe_3O_4 is so stable and unoxidizable that it is artificially produced on the surface of iron (*i. e.*, the "Barff" and "Bower" processes) as a durable coating for the purpose of preventing that metal from rusting.

Thirdly, FeO is somewhat magnetic, but Fe_2O_3 is very slightly so, if at all. According to Becquerel Fe_2O_3 is diamagnetic, and this is also stated by Mendeléeff and other authorities; though Plucker gives the specific magnetism of specular iron ore as 533 compared with 40227 for Fe_3O_4 and Sidot (*Compt. Rend.*, **67**, 175) has obtained an oxid exhibiting magnetic polarity by heating ferric oxid in an earthen tube placed in the magnetic meridian to a temperature not sufficient to fuse the oxid. A.

Frenzel also (*Jahr. f. Min.*, 1874, 685) obtained small rhombohedrons of iron glance, slightly magnetic, by igniting a precipitate of ferric hydrate; and Malaguti (*Ann. chim. phys.*, **69**, 214) states that a magnetic variety of Fe_2O_3 exists. These discrepant assertions may perhaps be caused by the fact that Fe_2O_3 when strongly heated gives off oxygen and is partially converted into Fe_3O_4. But be this as it may, the very slightly magnetic character of both FeO and Fe_2O_3 is as incontestable as is the highly magnetic character of Fe_3O_4. And as magnetism is conceded to be a physical property, dependent in some unknown way upon the molecular structure of bodies, the inference is irresistible that the molecules of iron and oxygen in Fe_3O_4 cannot be arranged in two groups, one of which has the structure of FeO and the other that of Fe_2O_3.

Fourthly, neither the hydrate of FeO nor that of Fe_2O_3 is magnetic. But the hydrate of Fe_3O_4 is attractable by the magnet, both when in the liquid from which it is precipitated and when in a dry state. Here, again, it seems idle to suppose that Fe_3O_4 exists as a combination of FeO and Fe_2O_3.

Fifthly, Lefort, (*Compt. Rend.*, **69**, 170) has succeeded in forming a definite salt by dissolving Fe_3O_4 in H_2SO_4 and evaporating the solution over H_2SO_4. This sulfate has the composition $Fe_3O_4.6SO_3.18H_2O$. But FeO combines with one molecule of SO_3 and Fe_2O_3 with three molecules of SO_3, so that the mixture $FeO + Fe_2O_3$ will combine with 4 SO_3. The combining power of Fe_3O_4 is therefore very different from that of $FeO.Fe_2O_3$.

Sixthly, if Fe_3O_4 be composed of a molecule of FeO joined to one of Fe_2O_3 it would seem that only one grouping is possible and that no isomer of the normal Fe_3O_4 can exist. But according to Moissan (*Ann. chim. phys.*, (5) **21**, 221) and Berthelot (*Ann. chim. phys.*, (5) **23**, 118) two varieties of Fe_3O_4 exist having distinct specific gravities, different solubilities in HN and different behaviors when exposed to heat. It is hence clear that Fe_3O_4 cannot have the constitution $FeO.Fe_2O_3$ unless moreover the isomerism be regarded as due to the presence of two varieties of Fe_2O_3.

Having now shown that no good reason exists for regarding Fe_3O_4 as being $FeO.Fe_2O_3$ and that many good reasons exist

against such a view, it remains for me to point out that another view of the molecular constitution is possible and preferable.

Let us, with Drechsel, F. W. Clarke, and some other chemists, regard iron as being a quadrivalent element, and let us dismiss the imaginary *ferrosum* and *ferricum* from our minds. Let us also consider oxygen as being virtually bivalent. And let us recognize the fact of the magnetic property of iron being impaired and well nigh destroyed by the union of the metal with oxygen; a fact which leads us to conclude that in any strongly magnetic oxid of iron some part at least of the metallic molecules must exist uncombined save with iron. The problem then arises whether any possible grouping of the molecules in Fe_3O_4 can comply with the requirements thus premised.

I submit that the following graphic formula is a solution of the problem, viz.:

```
O   —   O
|       |
Fe = Fe = Fe
|       |
O   —   O
```

Here each molecule of Fe is quadrivalent and each molecule of O is bivalent. One third of the iron, moreover, is uncombined save with iron and is, therefore, fully magnetic. We also see that a polymeric form is possible, viz.,

```
O — Fe — O — O — Fe — O — O — Fe — O
|   ||           ||           ||   |
|   Fe           Fe           Fe   |
|   ||           ||           ||   |
O — Fe — O — O — Fe — O — O — Fe — O
```

and this may well account for there being two varieties of magnetic oxid in both of which the proportions of iron and oxygen are as Fe_3 to O_4.

The slightly magnetic character of the protoxid may, I think, be shown by adopting the following formula,

$$= Fe = O$$

in which the iron molecule is not fully linked, and is, therefore, free to combine with another molecule of Fe O, thus

$$O = Fe = Fe = O$$

forming a somewhat magnetic body which is easily oxidized into the less magnetic ferric oxid, Fe_2O_3.

```
                O

O = Fe — Fe     O
```

and this, by further oxidation, becomes ferric anhydrid FeO_3, or Fe_2O_6:

```
        O         O

O - - - Fe ---- Fe - - - O

        O         O
```

It will be observed that the suggested constitution of Fe_2O_3 also admits of a polymeric variation, viz

```
O         O

Fe    O   Fe

Fe    O   Fe

O         O
```

and in accordance with this view it may be mentioned that two varieties of ferric oxid as well as of Fe_2O_3 are known. Indeed, as Mendeléeff very justly observes (Principles), all phenomena observed respecting ferric oxid (colloidal properties, various forms, formation of double basic salts) demonstrate that this substance like silica, alumina, lead hydroxid, etc., is polymeric; that the composition is represented by $(Fe_2O_3)_x$.

In conclusion, I would add that in the foregoing observations I have employed the concepts of molecule, valency and the like merely as customary useful aids to such an understanding and explanation of chemical and physical relations and phenomena as is possible in the present limited condition of our knowledge, and not as representing the esoteric facts of nature.

A FEW REMARKS ABOUT ALKALOIDAL ASSAYS OF DRUGS.*

By Chas. Caspari, Jr.

Unfortunately the determination of alkaloidal values of crude drugs and their galenical preparations has as yet not received that attention at the hands of the pharmacist which the importance of the subject demands, and even the pharmaceutical chemists employed by large manufacturing firms in this country appear thus far to have been satisfied with methods yielding results often of questionable accuracy. In both Germany and Great Britain our professional brethren are far in advance of us in this respect, and the inaccuracy and consequent undesirability of the gravimetric methods of determination of alkaloidal residues obtained in plant extraction have long since been recognized. Surely any analyst who may have taken the trouble of examining more closely the amorphous residue obtained in an assay of a drug, and weighed and reported as crude alkaloid, must have had his confidence in the method seriously shaken upon ascertaining that the amount of true alkaloid in the crude residue equals only from eighty to ninety per cent., or even less. It is argued by some that the determination of crude alkaloid in a drug or its preparation is quite sufficient, but it must be admitted that the value of assay methods depends upon the accurate determination of true alkaloid present; just as the amount of alkaloid may vary considerably in different samples of the same drug, so also may the proportion of impurities present in the crude residues vary in the same samples, and hence none of the gravimetric methods at present in use offer that security against error which is alone attainable by subsequent valuation of the crude alkaloids.

That such accurate valuation is feasible and extremely desirable has been demonstrated repeatedly, and as it involves merely the additional work of ten or fifteen minutes, it should never be omitted. Any one familiar with alkalimetry (and at the present day every educated pharmacist should be) can readily determine by titration the exact amount of true alkaloid present in a residue,

* From The Pharmaceutical Review.

which would otherwise be weighed as crude alkaloid and the results thus volumetrically obtained supply an assurance of accuracy which utterly fails in the gravimetric methods now employed.

As a matter of course, a little practice is requisite to become familiar with the end reaction, which is shown by a change in color, imparted to some suitable indicator, and which should be of the same shade for all operations. Cochineal is used almost exclusively as an indicator for titration of alkaloids in Germany but it has been found that in the presence of other coloring matter, often unavoidably mixed with the residue the end reaction is not very sharply marked. Dr Mew, analytical chemist of the Surgeon General's office at Washington first suggested a strong decoction of Brazil wood as an indicator for alkaloidal titrations, and in the writer's hands it has been found very efficient, the end reaction being much sharper than with cochineal, especially if the titration be conducted in dilute solutions.

As all interested in the assay of alkaloidal drugs are likely to be familiar with the different gravimetric methods pertinent to their merits and defects, it can be safely assumed that the operator will choose for isolation of the alkaloids the method likely to yield least contamination with coloring and other foreign matter; the crude residue thus obtained may be weighed and should then be dissolved in an excess of decinormal hydrochloric acid with the aid of gentle heat, noting the number of cubic centimeters of acid used, and making the solution up to fifty or one hundred cc. A sufficient quantity of indicator (Brazil wood decoction) is now added to show the pale yellow color produced by the acid and centinormal alkali then carefully added from a burette until the pale pink color (permanent) shows that a trace of alkali has been added in excess. The correct reading of the burette is now made and from it the amount of acid in combination with the alkaloid is calculated as follows: our hydrochloric acid being [illegible] we must multiply the number of cc used [illegible] as [illegible] alkali was employed and from this product subtract the number of cc alkali necessary to produce the permanent [illegible] color; the remainder will be the number of cc of [illegible] hydrochloric acid combined with the alkaloid and from this [illegible]

readily be calculated the actual amount of pure alkaloid present, by means of the proper multiplication factor.

This method of titration, involving the use of both acid and alkali solutions, appears preferable to the method suggested by some, of dissolving the crude alkaloid in ether or alcohol, and then titrating with $\frac{n}{100}$ acid alone after addition of a suitable indicator, since the color reactions are more sharply marked.

Another plan used by some analysts is to test the purity of the alkaloidal residue by solubility in dilute acid, and in case of incomplete solution filter out foreign matter, render solution alkaline and again wash out the alkaloid with ether or chloroform, dry and weigh; this method whilst preferable to simple weighing of the crude alkaloid, is far more laborious than that of titration and also less accurate, being subject to error by loss and otherwise.

In the case of drugs containing several alkaloids, the result can only be calculated as totals, our methods of assay thus far giving only imperfect and unsatisfactory separation, and the multiplication factor used must be found from the mean of the molecular weights of the alkaloids known to be present—thus for cinchona bark the mean of the molecular weights of the four alkaloids—quinin 324, quinidin 324, cinchonin 308, cinchonidin 308—would be 316, and hence each cc. $\frac{n}{100}$ hydrochloric acid will be equivalent to 0.00316 total alkaloids; for nux vomica the mean of the molecular weight of the two alkaloids, strychnin 334 and brucin 394 would be 364, and hence each cc. $\frac{n}{100}$ hydrochloric acid will be equivalent to 0.00364 total alkaloids.

The writer has experienced much satisfaction in the use of the titration method for determining the alkaloidal value of crude drugs as well as fluid and solid extracts, and would like to see the method more generally tried in this country and results reported in accordance therewith hereafter. A more complete series of experiments in connection with this subject is under way, and data will be published as soon as completed.

The use of the well-known Mayer's solution is still upheld by a few, but for quantitative determination of alkaloids this reagent is very unsatisfactory. Even in solutions of pure alkaloids the multiplication factor will vary in some cases as much as one or

two milligrams for each cubic centimeter, on account of the difference in strength of solutions; how great then must be the uncertainty when operating upon solutions of unknown strength of crude alkaloids; the end reaction is moreover in many instances very indefinite. As a qualitative reagent none is better or more convenient than Mayer's solution and it should be invariably employed to test the complete abstraction of alkaloids in any of the assay methods now used.

THE IVIGTÛT CRYOLITE MINE

By Chas. Hart

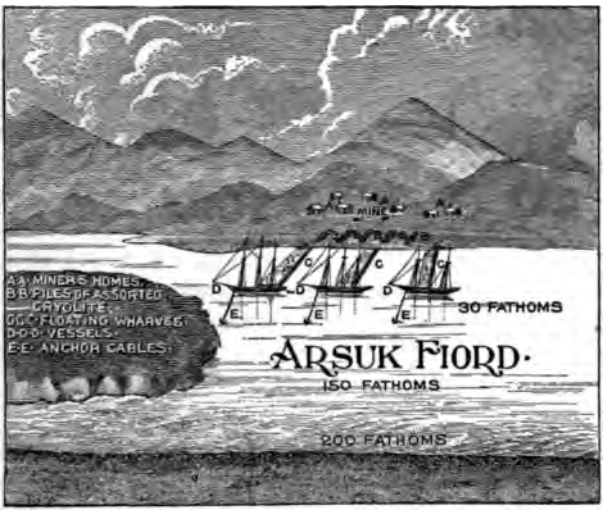
The mineral *cryolite* was found for the first time at Ivigtût in South Greenland, by a Danish whaler, who brought a piece of it to Copenhagen without stating where it came from. It was first described by Schumacher in 1795, and analyzed by Abildgaard, more correctly by Klaproth, who proved it to contain soda, the first time that this alkali had been found in the mineral kingdom otherwise than as common salt. Further analyses by Vauquelin, Berzelius, and Deville completely established the composition of the mineral. The original occurrence of the mineral in Greenland was discovered by Giesecke after long seeking (1806–1813). Up to 1840 it was only found in scientific collections, but in that year Professor Julius Thomsen at Copenhagen proved cryolite to be easily decomposed by lime both in the dry and in the wet way, and showed its application to the manufacture of soda. In 1864 he obtained an exclusive right; 1884 of mining for cryolite and working it up in Denmark for soda and alumina, this right was afterwards sold to a company. The first manufactory was built in 1857, at Copenhagen, the first large one still existing at Oeresund near Copenhagen. In 1865 and later on factories were erected at Harburg, Mannheim, Prague, Goldschmieden near Breslau and Warsaw. All the latter works have had to discontinue the use of cryolite since the Pennsylvania Salt Manufacturing Company at Natrona near Pittsburg, in 1865, obtained a right to two thirds of all the cryolite produced, *to maximum* [illegible] tons per annum, up to 1884. In 1886 it was proposed this mineral for the manufacture of aluminum.

On the whole, from 1856, when first whole cargoes were shipped, to 1886 [illegible] tons of cryolite were got, since 1886 about [illegible] per annum.

All cryolite comes from Ivigtut, from a valley on the south side of Arsuk Bay, where summer lasts three months. Some of the mineral is found below low water mark, but in a more impure state. On the mainland there is a bed of [illegible] square feet of white cryolite lying above impure mineral. Any mineral containing more than twenty per cent impurities is rejected. The purest is ten feet below the surface, which [illegible]

it becomes very dark, and at last almost black; but on igniting the latter, it also becomes white. The impurities are galena, copper-pyrites, spathic iron ore, fluor-spar, and lime-spar; the surface is covered with clay and sand. The working takes place chiefly from April to the end of December, and to a certain extent even during the remaining months.—*Lunge's Sulfuric Acid and Alkali*, 3, 53.

The cryolite mines of Greenland occur in latitude 62° N., and are reached by vessels through the Arsuk Fiord. This fiord is about one and one half miles in width, and at a point ten miles



up the mine is located. Ninety fathoms from the shore it has a depth of thirty fathoms, rapidly increasing in depth towards the other shore, where it is about two hundred fathoms. It is frozen from December until April, which prevents active operations, though about forty men are kept at the mines during this season of the year. The workmen are Danes, and every spring the steamer "Fox" brings enough men to swell the number to two hundred and fifty people. The steamer brings all supplies from Denmark and this is the only source of food, etc., upon which the workmen can depend, the freight vessels being prohibited from bartering. The "Fox" does tug duty for the freight vessels and in the autumn returns to Denmark with a portion of the

workmen. The boats engaged in this trade belong to McK and Dix, of New York, and are sailing vessels. Their names with the exception of the "Avigtut," named for the town and "Kryolith," named for the mineral, are derived from the constituent elements of cryolite, viz: "Argenta," "Sodium," "Salina," "Fluorine," "Iodine," "Silicon," "Alumina," and "Platina."

The last named vessel has probably been lost at sea in as much as it has been missing for some time. The vessels engaged in this trade have many hardships to endure, being threatened by floating ice. The time occupied in making a voyage from Philadelphia to the mines and return is not less than two months and sometimes it requires seven months to complete the trip. It is a rare thing for a vessel to make two trips in a season. The freights however, are good and there are no harbor dues in Greenland.

All the cryolite is imported by the Pennsylvania Salt Manufacturing Company and it is delivered at Greenwich pier for which the ship company receives 37s. 6d. freight. The cost of a ton of cryolite delivered at Philadelphia is about $38.00. The Danish government charges an export duty upon the mineral. This duty is computed by one of their representatives at the place of delivery. The contract calls for 10,000 tons annually, but this year the amount probably will be but half this on account of the ice. It is estimated that 8,000 to 9,000 tons have been obtained annually for the last twenty-eight years. The value of the product exported from 1867 to 1886 inclusive is about $1,[illegible]. Of the quantity mined a portion is sent to St. Petersburg. The entire product is under the control of a company in Copenhagen although the Pennsylvania Salt Manufacturing Company controls the American trade.

The mining of cryolite is entirely in charge of Danes and the methods in use are practically the same as were in vogue when the mines were first worked. The mine is eighty seven feet in diameter and has a circumference of three hundred and sixty five feet. It is ninety two feet from the river bank and was first worked at four feet above sea level; it has now reached a depth of 185 feet. In blasting very small charges are used. The fragments are loaded on cars of five tons capacity; these cars are drawn up an incline by means of an endless chain

The cryolite is assorted and piled in five heaps upon the earth between the mine and the shore. The impurities amount to twenty per cent. The contract requires that ninety per cent. of the material shipped shall be cryolite. In bringing it to this state of purity a great deal is lost, in amount about 2,000 tons annually. This waste material is used in making ground about the mine as a protection against the fiord and the water gathered from the surrounding mountains. The floods gave so much trouble during the past season as to cause fear of the necessity of abandoning the mine. The causes of heavy loss in assorting the mineral are two in number: (1) The occurrence of impurities in large lumps, which take with them considerable cryolite; (2) The shipment of cryolite by cars after its arrival in America, thus losing fine particles of cryolite. In preparing the mineral for the vessels, the large masses of impurities are thrown away, and also the fine particles of cryolite. If either were left in the cargo the mineral at Natrona would have a percentage of impurities higher than allowed. Only large pieces of cryolite are shipped. This method entails a large amount of waste. Although the consumers are willing to take the product just as it comes from the mine, the Danes prefer to keep the contract as it stands.

The vein appears to widen as the mine deepens. For the sake of safety, on this account, pillars of cryolite are allowed to stand at intervals of thirty feet; the columns are eight feet in diameter and support the surrounding rock. The vein of cryolite separates from the rock enclosing it with a clean fracture, so that its boundary is easily distinguishable. There appears to be no decrease in the quantity of the cryolite, but at the present depth of the mine the quality is inferior.

When the mines are closed for the winter, salt water is run in from the Arsuk fiord through sluices until it is filled to about one-third its depth. It is allowed to freeze and in the spring when work is resumed the ice is removed in the cryolite cars and the water pumped out.

When the cryolite is piled upon the wharf it remains until the vessels come for it. Extending from the land are floating wharves; one end is attached to the rocks in such a way that the other end

floats about it as a center. These wharves are three in number. It is over these that the men wheel the cryolite to the vessels. The vessel having been towed into place by the Fox [illegible] anchor and also fastens to the shore by cables. The wharf is fastened and the loading begins. After the vessel gets its cargo it is towed out by the steamer.

DETERMINATION OF QUININ IN CINCHONA BARKS.*

BY [illegible] SCHMIDT OF [illegible]

[Translated from the original article published in [illegible]]

Although numerous methods have been published for the quantitative determination of quinin in cinchona barks, they have the disadvantage of either being too tedious and complicated or of yielding unsatisfactory results.

The method for obtaining quinin tartrate free from color so as to enable determination of the quinin by polarization is still kept a profound secret, and I would suggest the following method which has given me very satisfactory results. Twenty grams of air-dried finely powdered cinchona bark are placed in an Erlenmeyer flask together with ten cc. ten per cent. ammonia water, twenty cc. ninety per cent. alcohol and 150 cc. ether, and the mixture macerated for twenty-four hours with frequent and active agitation.

100 cc. of the clear liquid are transferred to a beaker, [illegible] seven cc. water and three or four cc. normal hydrochloric acid are added, and the liquid set aside for twenty-four hours [illegible] spontaneous evaporation. Any alcohol and ammonia still remaining in the liquid are driven off by heat on a water bath [illegible] necessary, an additional quantity of normal hydrochloric acid added so as to obtain a neutral or only faintly acid solution. If the liquid be too strongly acid it should be neutralized by a [illegible] of cinchonin, but under no circumstances should ammonia or potassa solution be used for the purpose.

In case very high grade *Cinchona* barks are under examination it may be necessary to add as much as one or two cc. normal acid additional, so as to insure complete solution of the alkaloids.

The quantity of liquid finally remaining after evaporation [illegible]

* From The Pharmaceutical Review.

alcohol and ammonia should not be less than fifteen cc.; greater concentration and acid reaction frequently cause decomposition.

After cooling, the liquid is exposed to the air for some time until it becomes clear, a reddish brown coloring matter usually subsiding; when clear it is filtered and to the filtrate two or three gms. potassium sodium tartrate (Rochelle salt) are added, the mixture warmed for fifteen minutes on a water-bath and set aside for twenty-four hours. The precipitated tartrates are separated by filtration, washed with as little water as possible and drained.

In order to make sure that all quinin and cinchonidin have been precipitated as tartrates, the mother liquor may be warmed again with a small portion of Rochelle salt, whereupon it should remain clear.

The mother liquor and washings should be measured and (according to Moens) 0.0008 gm. for each cc. of the former, and 0.0004 gm. for each cc. of the latter added in the final calculation for quinin.

The washed tartrates are now dissolved in water with the aid of hydrochloric acid, avoiding a large excess of the latter; the solution is treated repeatedly with ether in a flask, as long as the ether becomes colored and continues to leave a residue on evaporation; by means of sodium hydroxid solution the alkaloids are precipitated and dissolved in ether with aid of gentle agitation, the treatment with ether being repeated until all alkaloid has been brought into solution; the ethereal liquid is finally evaporated and the residue dried to constant weight at 100°–110° C. and weighed. If cinchonidin be present in the alkaloid it will be detected by the white crystalline powder present in the residue.

In order to ascertain the exact amount of quinin present, the alkaloidal residue is treated with a saturated solution of cinchonidin in ether, which dissolves all the quinin, but leaves the cinchonidin unaffected. As far as known, ether saturated with cinchonidin, when added to a mixture of cinchonidin and quinin, takes up only the latter, without losing, at the same time, its own cinchonidin; any residue so remaining is then quickly washed with a little pure ether and carefully dried to constant weight. The difference between the weight of the final residue and that of total alkaloids first obtained is calculated as quinin.

SPICA'S METHOD FOR THE DETERMINATION OF PHOSPHORIC ACID.*

BY CARL ARNOLD AND CONRAD WEDEMEYER

In the *Gazz. chim. ital.* **12**, 117, Matteo Spica has proposed a new method for the volumetric determination of phosphoric acid. This method is founded upon the complete precipitation of phosphoric acid from neutral solutions by potassium ferric sulfate as ferric phosphate. The operation must be conducted in the cold and the phosphoric acid solution must be free from foreign salts; salicylic acid is used as the indicator.

If potassium ferric sulfate solution is added drop by drop to a phosphate solution containing the indicator, the precipitate which forms has a violet color which disappears on shaking. As the end of the reaction approaches, the coloration becomes more intense, and the whole mass takes a violet tinge and so renders it difficult to detect an excess of ferric alum. Even if we wait until the precipitate settles the end point is difficult to fix since the liquid has the violet coloration as well. On heating the coloration disappears unless a great excess of ferric alum is present. The difference between the amounts of ferric alum needed in the cold and at a boiling temperature is equal to twenty cc. sodium ammonium phosphate solution containing one cc. corresponding to about two cc. of a saturated solution. By several comparative determinations the equivalent value of the ferric alum may be determined as compared with the easily purified microcosmic salt.

A solution of orthophosphoric acid neutralized with sodium hydroxid contained, according to the molybdic acid method, four agreeing determinations 6.[illegible] per cent phosphorus pentoxid, according to Spica's method in the cold 6.[illegible] and 5.[illegible] when the end point was determined in a boiling solution. [illegible] per cent phosphorus pentoxid. It more of the indicator [illegible] the end point is still more difficult to determine.

Experiments with other indicators gave still less satisfactory results. To determine phosphoric acid in Thomas slag, Spica directs that the slag be evaporated with concentrated sulfuric acid and the [illegible] on a solution free from [illegible]

* [illegible]

num and manganese the phosphoric acid taken up with absolute alcohol. This method of dissolving suffers from the known error that the separated sulfates contain phosphoric acid; and only by the use of a large amount of alcohol can all the phosphoric acid be brought into solution.

The residue from five gms. Thomas slag treated with sulfuric acid and extracted with 500 gms. absolute alcohol was treated with nitric and hydrochloric acids; the phosphoric acid determined by the molybdic acid method was found to contain 0.61 per cent. P_2O_5. Another slag, treated in the same way but extracted with 1000 grams absolute alcohol, contained 0.29 P_2O_5 in the residue.

In consequence of this unavoidable source of error on the one hand, the total amount of phosphoric acid cannot be determined. On the other hand, by slow washing with alcohol a part of the iron oxidizes and becomes soluble in the alcohol. If such a solution is neutralized the phosphoric acid is precipitated and the solution becomes worthless for the determination. A Thomas slag which gave 17.88 per cent. phosphorus pentoxid as the mean of four determinations by the molybdic acid method, gave as a mean of eight determinations by Spica's method 16.59 per cent. phosphorus pentoxid. A slag which contained 17.63 per cent. phosphorus pentoxid gave by Spica's method only 15.84 per cent. phosphorus pentoxid.

Another slag containing, in mean, 9.18 per cent. P_2O_5 gave by Spica's method when extracted with a large amount of alcohol 8.86 per cent. in mean.

As a result of this examination the conclusion is warranted that the new process is scarcely likely to find its way into the laboratory, because it is (1) dearer, (2) requires too much time, and (3) does not give accurate results.

NEW BOOKS.

Venable's Qualitative Analysis.*—The works on qualitative chemical analysis are legion, but this little book, which Dr. Venable originally compiled for use in his own classes, will

* A Course in Qualitative Chemical Analysis. By F. P. Venable, Ph.D., F. C. S., Professor of Chemistry in the University of North Carolina. Second edition, pp. 53. New York: University Publishing Company.

commend itself readily to the teacher of the subject of which it treats. The introductory tables for blowpipe work and the concluding tests for acids are especially valuable. Credit is given in this second edition to Prof. F. P. Dunnington, of the University of Virginia, for assistance. Only three groups of bases are recognized: *First*, those precipitated from acid solutions by hydrogen sulfid; *second*, those not precipitated by hydrogen sulfid but by ammonium sulfid; and *third*, those which neither hydrogen sulfid nor ammonium sulfid will precipitate. It is perhaps open to debate whether it is not easier to teach by dividing into a larger number of groups. The explanations of chemical reactions are clearly made and the general impression conveyed by a perusal of the book is that a careful use of the same by the student will prove it to be what it was written for "not an assistance in mechanical work but an incentive to thought and reflection."

NOTES

E. A. de Schweinitz has been elected Lecturer on Chemistry in the Medical Department of Columbian University, Washington, D. C., Charles E. Munroe, Professor of Chemistry, and H. C. Bolton, non-resident Lecturer on the History of Chemistry in the same institution.

Mr. S. A. Ford, chief chemist of the Edgar Thomson Steel Works, at Braddock, has resigned his position. Ill health was ostensibly the cause of the resignation, and General Superintendent Gayley, of the plant, accepted it. Mr. Ford has held the responsible position of chief chemist for the past fourteen years.

Reference was made in the August number of the Journal (**6**, 422, foot note) to the trouble experienced in the laboratory of the New York Tartar Company by fungoid growths appearing in a sulfuric acid. The normal solution apparently was not subject to this decomposition. Mr. C. J. Lawler, chemist for the Royal Baking Powder Company, informed me recently that he had experienced the same trouble, but had found a simple way of obviating it, viz., by adding a few drops of chloroform per liter to the freshly made standard solution of sulfuric acid.

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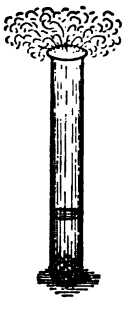
THE

Journal of Analytical and Applied Chemistry.

A MODIFICATION OF SCHÜTZENBERGER'S METHOD FOR DISSOLVED OXYGEN.

BY AUGUSTUS H. GILL, PH.D.

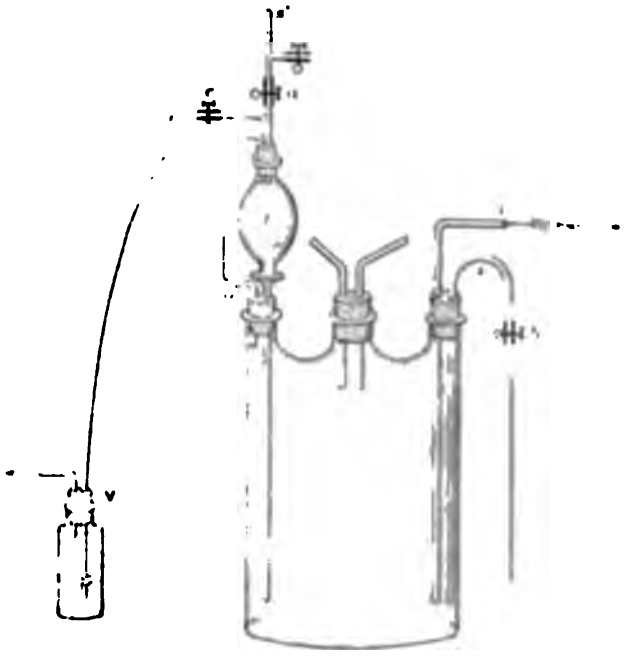


IN the course of the investigation of the water supply as carried on by the Massachusetts State Board of Health during the winter of 1887 and 1888, it became desirable to estimate the oxygen dissolved in the various waters; the only available method at that time was that of Schützenberger, which was somewhat modified and yielded very satisfactory results.

The changes in apparatus and method are briefly these: (1) arrangement of apparatus so that the water can be measured and introduced into the Woulff bottle out of contact with air; (2) the use of a gentle pressure of hydrogen to exclude air from the Woulff bottle when not in use, and from the hyposulfite bottle and burette; (3) the use of indigo free from indigo-rubin, enabling sufficient indigo to be used to combine with all the oxygen in the water and the end point to be sharply read; (4) the titration being made with the same quantities in the Woulff bottle and in the same time. The apparatus will be understood from the figure.

One neck of a liter Woulff bottle has passed through its stopper the inlet tube for hydrogen *i* and the siphon *s* for emptying the bottle; the second carries the tips of the indigo and hyposulfite burettes; the third holds the separatory funnel *f* and the outlet for hydrogen *o*. The stopper of the funnel *f* carries three tubes, one of which is connected with the outlet *o* from

the Woulff bottle, the second with the valve bottle V [illegible] as the final outlet for hydrogen, the third with the lower [illegible] the siphon *s'*.



The other limb of this siphon extends half way down [illegible] bottle of water to be analyzed. It is provided with a [illegible] of filling.

Method of Procedure. The Woulff bottle and funnel are completely filled with water, the burettes filled, the [illegible] closed, and the cock of the hydrogen generator and the spring clip *b* opened. The water is displaced through [illegible] and the whole apparatus thus filled with hydrogen. The spring clip [illegible] shut and [illegible] opened, allowing a slow current of hydrogen [illegible] through the apparatus.

Four hundred cubic centimeters of the water to be tested are introduced through the funnel into the Woulff bottle, the funnel

re-filled and twenty-four cc. indigo added from the burette. The deep blue color is now discharged by cautious addition of hyposulfite, the amount being noted, until the pure yellow color remains permanent for one minute by the watch. The two hundred cubic centimeters in the funnel are now run in and the blue color discharged, the same end point being taken as before. The difference between the amount of hyposulfite last used and that previously used, represents the amount oxidized by the free oxygen in the water.

Close the spring-clip *c*, open *a* and *b*, the water in the Woulff bottle will be forced out through *s* by the pressure of water filling the funnel and received in a 250 cc. measuring cylinder. When *f* is full, close *a* and when the amount of water in the cylinder is equal to 208 cc.,* plus the amount of hyposulfite added, close *b*. This will leave, within a few cubic centimeters, the same amount of liquid in the bottle for each titration,—a point of importance to be observed. Eight cubic centimeters of indigo are now added, and the liquid decolorized, the end point being taken as above, the amount of hyposulfite being noted. The two hundred cubic centimeters of water in the funnel are now added and the titration repeated as above described. A mean of the amounts of hyposulfite is now taken. The hyposulfite can be standardized against fully aerated water as recommended by Dupré,† or by ammoniacal copper sulfate solution, according to Schützenberger.‡ The aerated water is prepared by shaking pure water in a shaking machine, renewing the air in the bottle by sucking in the outside air.

RESULTS.

(1) 200 cc. water required 7.95, 8.00, and 8.10 cc. hyposulfite. Average, 8.05 cc. 1 cc. hyposulfite = 0.0224 cc. oxygen, ∴ cc. oxygen in the water is $8.05 \times 0.0224 \times 5 \times \frac{3}{5} = 5.410$ cc. By eudiometric analysis of dissolved gases, boiled out according to Reichardt's Method, (*National Board of Health Report*, 1882, p. 284). 5.772 cc. oxygen were obtained.

(2) 200 cc. required 7.80, 7.85, 7.85 cc. hyposulfite. Average, $7.84 \times 0.0224 \times \frac{3}{5} \times 5 = 5.302$ cc. By gas analysis, 5.365 cc.

(3) 200 cc. required 6.75, 6.55, 6.66, 6.62 cc. hyposulfite. Average, $6.65 \times 0.0224 \times \frac{3}{5} \times 5 = 4.467$ cc. By gas analysis, 4.4512 cc.

* Eight cc. equals $\frac{1}{5}$ the indigo added which is taken out by the 200 cc. of water already siphoned out, leaving 400 cc. behind.

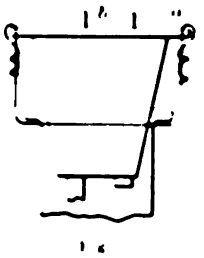
† Analyst. 10, 156. ‡ Bull. Soc. chim. (Paris), 20, 145.

The hyposulfite was standardized against aerated water at a known temperature and ammoniacal copper sulfate identical results being obtained. The factor as recommended by Ramsay and Williams* was found to give a closer approximation than as recommended by Dupré.†

In reporting results, if the plan suggested by Dupré be adopted "in percentage of possible amount," care must be taken that the temperature which is used as a basis be that of the river or pond *at the time of taking the sample*. I have found that the temperature of imperfectly aerated water can be raised or lowered ten degrees especially when tightly stoppered, without affecting the amount of oxygen; that is, the absorption or evolution of oxygen lags behind the changes of temperature. Nearly every one who has used the process, has recommended covering the hyposulfite solution with a layer of oil to prevent the absorption of oxygen, but this is worse than useless, as Gniewosz and Walden have shown that oils absorb oxygen more readily than water.‡

Potassium pyrogallate, in my hands, did not give satisfactory results as a means of protection to the hyposulfite solution. I connected the top of the burette with the hydrogen generator, siphoning in the hyposulfite at the bottom. The hyposulfite stock bottle is also protected in a similar manner and covered with a dark cloth to keep out the light.

When the apparatus is not in use the spring clip is closed, the cock of the hydrogen generator being open, which keeps a constant outward pressure of hydrogen in the apparatus effectually excluding the air. This necessitates joints which are hydrogen tight, and if rubber stoppers are used throughout and wired down as in Fig. 2, no difficulty will be experienced.



a represents a brass plate which is placed over the top of the cork and wired down, passing around the neck of the bottle. If wired down after the manner of bottles containing effervescent drinks, the pressure of the wire causes the rubber to spread and a leak ensues.

* [illegible] this journal [illegible]

If a funnel cannot be procured which delivers exactly 200 cc., one slightly larger may be used, and made to deliver exactly that amount by dropping in an Erdmann's float, or bits of glass tubing until the requisite amount of water has been displaced by these articles.

The Woulff bottle and hydrogen generator may be conveniently placed on a shelf attached to the wall of the laboratory, a higher shelf being provided, upon which are the indigo and hyposulfite stock bottles connected by siphons with the burettes.

Preparation of Indigo Solution.—Dissolve eight grams sublimed indigotin, which has been treated with ninety per cent. alcohol until free from indigo-rubin, shown by giving little or no color to the alcohol, (the indigo-rubin masks the end point), in 120 grams strong sulfuric acid. The sulfindigotic acid is salted out, brought upon a filter, and washed with a little salt solution. It is now dissolved in two liters of water, made faintly alkaline with sodium carbonate or hydrate, and filtered.

Hyposulfite Solution.—Dissolve ten grams of the commercial "bisulfite of soda" in a liter of water, saturate with sulfurous acid, and treat in the usual way with zinc.

The hydrogen is best prepared from zinc and sulfuric acid, and should be passed through a strong solution of hyposulfite, strong sulfuric acid, and over stick potash. The exit tube should be provided with a valve to prevent water being forced into the potash.

The writer is well aware that almost the same modification of this method was published by Roscoe and Lunt in the *Journal of the London Chemical Society*, August, 1889, but would say that the manuscript from which this article is printed, was in its present form, ready for publication in June, 1888, a full year before the appearance of the article to which reference is made. The statement made with reference to the "lagging behind" of oxygen was deemed, however, insufficiently substantiated, and owing to absence abroad the necessary experiments could not be made until recently.

UPON THE DIFFICULTY WITH WHICH WATER PARTS WITH ITS DISSOLVED OXYGEN

By Augustus H. Gill, Ph.D.

In the preceding article, attention has been called to the "lagging behind" of oxygen, or the difficulty with which it leaves nearly saturated solutions when they are heated considerably above the saturation point; this paper considers the subject more in detail.

As is well known, with a saturated solution of a solid a depression of the temperature causes its almost immediate precipitation, more especially if it be shaken, or particles of the same are in contact with it; with gases, the molecules of which are so free to move, one would suppose the same phenomena would occur, except with greater ease and rapidity. As Ostwald says, "by rise in temperature liquids are completely freed from dissolved gases." This, however, takes place very slowly, as is shown by the following experiments.

Method of Procedure.—The calibrated bottles holding about 250 cc. were filled from the laboratory tap by a rubber tube passing to the bottom of the bottle; the water being previously allowed to run for some time to ensure a representative sample. In taking this sample, a quantity of water was allowed to run sufficient to fill the bottle about sixteen times. The temperature was taken by placing a delicate thermometer in the bottle as it was being filled. The method followed for the determination of oxygen was that of L. W. Winkler.* After being drawn some of the bottles were left standing open in the room, the temperature of which was 22°, and others also open placed in the water bath at 30°.

TABLES I

[illegible]	[illegible]	Oxygen	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]		
		[illegible]	[illegible]		
		[illegible]	[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]		[illegible]

[illegible]

By heating then four hours to 30°, the water was still supersaturated, less than four per cent. of oxygen being given off; this was even less than was given off by heating seven hours to 22°, it requiring twenty-four hours to bring it down to the point of saturation.

In Series II the oxygen seemed to leave the water even more slowly, 6½ hours exposure at 30° causing a loss of but about six per cent., and forty-eight hours exposure at 22° causing but 2.3 per cent. loss.

SERIES II.

Time of heating.	Temp., ° C.	Oxygen, cc.	% basis of 9°.	% basis of 22°.	% basis of 30°.
	9	6.823	84.61		
		7.016	87.02		
		6.955	86.26		
48 hours	22	6.639	82.33	108.6	
		6.832	84.72	111.8	
6½ "	30	6.528	80.76		124.3
		6.416	79.58		122.1

The foregoing experiments were performed with eighty-five per cent. aerated water; ninety-two per cent., as might be expected, gives up the oxygen rather more slowly as the following series indicates:

SERIES III.

Time of heating.	Temp., ° C.	Oxygen, cc.	% basis of 5.9°.	% basis of 22°.
	5.9	8.031	92.33	
		8.071	92.80	
24 hours	22	7.772	89.32	127.2
		7.643	87.86	125.0
48 "	22	7.088	81.47	116.0
		7.083	81.42	115.8
7½ "	33	7.451	85.65	
		7.405	85.22	

The results of this experiment confirm the observations made in the winter,—that the waters then received being cold and nearly saturated, hold on to the oxygen very tenaciously.

To ascertain if the shape of the vessel exercised any influence upon the rapidity with which the oxygen was given off, experi-

ments were made, using bottles with necks one and one half inches in diameter instead of half an inch. The water was exposed for twenty-four hours at 22°.

Percentage of aeration	Bottles with 1½ inch necks	Bottles with [illegible] inch necks
80.30	83.04	[illegible]
80.66	83.85	[illegible]
92.33	79.37	[illegible]
92.80		

These show, as was expected, that the greater the surface the more rapidly the oxygen leaves the liquid, making a difference of about five per cent.

The results given in these experiments do not indicate particularly closely agreeing determinations, by no means within the limit of accuracy of the method. This is due to the fact that it is well-nigh impossible, even after the water has been allowed to run from ten to fifteen minutes, to draw consecutive samples of water that are of the same composition. Mr. F. S. Hollis, one of the water analysts of the city of Boston, has observed this same fact, and collects the samples by allowing the water to run through a T tube into each bottle. In the following series, the bottles were all filled from the same large bottle of water, the contents of which had been thoroughly mixed.

Time of heating	Temperature	Oxygen	[illegible]	[illegible]	[illegible]
		[illegible]	84.34		
		[illegible]	[illegible]		
		[illegible]	[illegible]		
		[illegible]	[illegible]		
24 hours	22	[illegible]		[illegible]	
[illegible]	[illegible]	[illegible]			[illegible]
		[illegible]			[illegible]

This shows a much better agreement of the results among themselves than those of series I, II, and III, and substantiates the conclusions there drawn.

That water as regards oxygen contents does undergo changes in the pipes is well shown in the following series. During the night, there had been very little drawn; it was allowed to run for

five minutes, and samples taken consecutively at five different times.

Time.	Temp., °C.	% of aeration.	Time.	Temp., °C.	% of aeration.
9.02 A. M.	27.5	46.73			
9.07 "	7.5	80.86	9.37 A. M.	5.5	82.31
9.17 "	6.0	80.30	10.07 "	5.5	83.80

Another experiment showed, after the water had been running fifteen minutes, 89.4 per cent. aeration, after running thirty minutes 92.5 per cent. This would indicate that the composition of a water, coming through any considerable distance of small pipe, as regards oxygen contents, is not constant until perhaps 200 liters have been drawn, or it has been allowed to run from a half inch faucet for half an hour.

The results of the foregoing experiments would indicate:

(1) The necessity of knowing the initial temperature of a water in order to report "percentage of saturation."

(2) That a water can be heated 10° above its saturation point for twenty-four hours—in some cases forty-eight hours—without entirely giving up the excess of oxygen; this takes place with greater rapidity from a wide mouthed vessel.

(3) That it is impossible to draw two consecutive samples of water from the same faucet with exactly the same oxygen contents. This variation is undoubtedly due to changes of pressure in the pipe system; possibly this statement may be true of other constituents.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
LABORATORY OF SANITARY CHEMISTRY AND GAS ANALYSIS.
NOVEMBER, 1892.

ON THE DETERMINATION OF WATER AND OF FREE FATTY MATTER IN SOAP.*

BY J. ARTHUR WILSON.

The usual method of determining water in soap by drying a weighed quantity of the sample, cut into thin shavings, at increasing temperatures up to 110° C., does not give the most accurate results, and, besides, is frequently very tedious. Watson Smith's modification has in my hands not been successful,

* Chem. News, 66, 200.

especially with highly watered soaps. The free fatty matter is also very frequently considerably in error when done by the old process, especially when extraction is continued for only [illegible] hours.

By the methods to be now described, the time required for both determinations is materially shortened and greater accuracy obtained.

Water Determination.—About 2.5 gms. of the sample is weighed out in a thin flat-bottomed porcelain dish three inches diameter and 0.5 inch deep (such as are used for total solids in milk analysis). It is gently melted and five cc. of absolute alcohol added, and the dish warmed on the water bath till soap is dissolved; whereupon about ten gms. of ignited sand is added and incorporated with the dissolved soap; the dish is afterwards placed on the water bath for one hour. Five cc. of absolute alcohol is then poured over the sand, then the dish is placed in the air bath at 100-105° C. till constant weight is attained. With ordinary soaps, and the use of the improved air-bath this will be in about three hours; whilst highly watered soaps require about five or six hours.

Determination of Free Fat.—The residue from the water determination is ground up in a glass mortar and transferred to the Soxhlet tube, and exhausted with re-distilled petroleum ether, two hours being sufficient under these conditions. The Soxhlet tube should have a mercury seal and ground joints in place of corks.

Modification.—If the sample contains free caustic alkali (as seen by dropping a little phenol phthalein on a clean surface of the sample), the residue from the water determination cannot be used for the determination of the free fat, on account of the saponification of the latter by the free alkali. In such a case the ordinary method of determining the water is adopted, but it is not necessary to prolong the drying more than [illegible] hours. The dry residue is then ground up with ten grams of sand, transferred to the Soxhlet, and exhausted as before.

The improved process for free fat determination gives higher results for the same reason that the paper coil and plaster [illegible] do in milk analysis.

NOTE ON THE DETECTION OF BROMIN, CHLORIN, AND IODIN IN THE SAME MIXTURE.

By F. P. Dunnington.

In the article of Mr. Lyman F. Kebler (this Journal **6**, 569) upon this subject, he gives a resumé of the methods employed and alludes to the necessity of employing soluble haloid salts for the most satisfactory of the processes.

For some years I have with satisfaction used a method which I have recently put in print in the second edition of Professor F. P. Venable's *Qualitative Analysis*, 1892, page 46. It is as follows: From a solution acidified with nitric acid precipitate the silver salts of these acids with silver nitrate solution; having filtered off and washed this precipitate, treat it in a test glass with a few drops of very dilute sulfuric acid and a bit of zinc; when the dark spongy mass of metallic silver is formed, pour off the solution of the zinc salts and examine it for iodid, bromid, and chlorid by the method of Professor Edward Hart.

University of Virginia, Dec., 1892.

SULFUR IN COAL AND COKE: RESULTS BY ESCHKA'S METHOD VS. THOSE BY HUNDESHAGEN'S METHOD.*

By Jas. O. Handy.

Eschka's Method (Pittsburgh Testing Laboratory practice). One gram fine coal, one gram pure magnesia (Baker and Adamson's), and one-half gram C. P. sodium carbonate (Baker and Adamson's), are mixed thoroughly and heated in a 100 cc. platinum dish, over a Bunsen burner. Begin with the flame just touching the dish. Raise the heat gradually so that in fifteen minutes the dish is red hot. Stir frequently with a platinum wire, until the carbon has burned away. Allow to cool. Brush the contents off the dish into a 200 cc. beaker, add 100 cc. of water, 15 cc. of bromin water, and boil for five minutes. Filter and wash well with hot water. Make the filtrate up to 250 cc.,

* Read before the chemical section of the Engineers' Society of Western Pennsylvania.

add hydrochloric acid until just acid and boil off the bromin precipitate with barium chlorid as usual. $BaSO_4 \times 0.13734$ [illegible] No sulfur has been found in Baker and Adamson's magnesia [illegible] sodium carbonate and no correction is required.

This method has been used by us, essentially in the present form, for the past four years, and has given satisfaction.

Hundeshagen's Method (as described in this JOURNAL 6, No. [illegible] p. 385) is essentially as follows: One gm. coal and two gms. of a mixture of two parts pure magnesia and one part pure potassium carbonate are placed in a platinum dish and mixed. The remaining operations are practically the same as described above under Eschka's method.

In our experiments on samples of coal from different sources we obtained the same results by the Eschka method and the Hundeshagen method. We noticed no greater rapidity of burning in the Hundeshagen than in the Eschka process.

COMPARISON OF ESCHKA AND HUNDESHAGEN PROCESSES.

Sulfur in Coal.

Number	Source	Fixed Carbon	Volatile Matter	[illegible]	[illegible]
10170	Westmoreland Co.	55.18	33.40	[illegible]	[illegible]
10516	Pittsburgh vicinity	52.02	[illegible]	[illegible]	[illegible]
10517		[illegible]	31.02	[illegible]	[illegible]
8825	Unknown	48.83	[illegible]	[illegible]	[illegible]
9304	Charters	51.48	[illegible]	[illegible]	[illegible]
9305	Youghiogheny	54.46	35.32	[illegible]	[illegible]

Sulfur in Coke.

Sample No. [illegible] sulfur E. process [illegible] per cent; H. process [illegible] per cent.

These experiments effectually disprove Hundeshagen's assertion that sodium carbonate in the Eschka mixture is [illegible] as efficient in retaining the sulfur of certain coals as is the potassium carbonate in his mixture. It may be that none of the samples of coal which we examined contained any sulfur in organic combination. It is hardly probable that such was the case.

It is certain from our experiments that the compounds of sulfur with the bases in the Eschka method are as stable [illegible] heated as are those formed in the Hundeshagen method.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF LEAD.*

By F. C. Knight.

A technical method for the volumetric determination of lead, requiring but an ordinary amount of manipulation and occupying a short space of time, has long been desired. A number of such methods have been suggested from time to time that promised more or less success. Of these there are but two which give results that are sufficiently accurate even for technical work, a brief outline of which will be given.

The first, which is the more practical, consists of neutralizing the nitrate of lead solution with ammonia or carbonate of ammonia, then adding an excess of acetate of sodium, and effecting the titration with a standardized solution of bichromate of potassium, the end reaction being indicated by a red coloration on bringing a drop of the lead solution in contact with a drop of a neutral solution of nitrate of silver. With careful manipulation this process yields good results. The greatest objection to be brought against the method is the uncertainty of the complete precipitation of the lead as the chromate if special precautions are not observed; the length of time involved in the process, and, finally, the ease with which the end point of the reaction can be overstepped.

The other method consists in precipitating the lead as carbonate from its solution, dissolving the precipitate in a measured quantity of normal nitric acid, to which then a neutral solution of sulfate of sodium is added. The sulfate of lead is precipitated and an equivalent amount of nitrate of sodium formed. The free nitric acid is subsequently determined with a normal alkali solution, the lead percentage being calculated from the observed difference between the original amount of nitric acid used, and that found to be still free. This plan requires the lead solution to be quite free from other elements, for which special precautions are necessary, and the length of time involved in the operations quite unfits the process for technical laboratories.

*Read before the Colorado Scientific Society, Nov. 7, 1892. Communicated by the author.

There is another method which has been lately described which, while not volumetric, appears to offer great advantages over the preceding ones. It consists in dissolving the sulfate of lead in an ammonium chlorid solution, and precipitating the lead from the same in the metallic form by means of sheet aluminum the lead finally being weighed. The results appear to be very accurate. The existing prejudice in technical laboratories against any method which involves a gravimetric determination will, however, operate as a bar against its general introduction if a method equally as accurate, or sufficiently so for all purposes but volumetric, can be found.

The method about to be described is offered in the hope that it will meet the required conditions. It is based on the formation of oxalate of lead, the decomposition of this salt by sulfuric acid, the determination of the liberated oxalic acid by permanganate of potassium solution, and the calculation of the lead percentage from the amount of oxalic acid with which it was originally combined.

It is not claimed that the idea on which this scheme is founded is new; in fact, a method along similar lines was proposed by Hempel, it being also stated by him that the results obtained were not absolutely accurate owing to the solubility of the oxalate of lead, which error, however, could be reduced to within the limits of one per cent by careful manipulation.

Fresenius, in discussing the solubility of oxalate of lead in water, states it to be distinctly greater than that of sulfate of lead the solubility being still further increased by the presence of ammonia and ammonium salts.

A large number of experiments instituted for the purpose of determining how the solubility of the oxalate of lead in water could be overcome showed eventually that while it could not be entirely nullified it could be reduced to its minimum by effecting the precipitation from an aqueous solution of the lead salt containing about an equal bulk of ninety-five per cent alcohol, only the slightest traces of lead remaining in solution under such a condition. Further experiments demonstrated that the precipitation was equally complete in the presence of free oxalic acid which had been added to the alcoholic solution.

To a neutral solution of nitrate of lead measuring about twenty cc., an equal volume of ninety-five per cent. alcohol and five cc. strong acetic acid were added, and the lead precipitated by oxalic acid. The precipitate was filtered, well washed with hot water, and the filtrate saturated with hydrogen sulfid gas. A slight brown coloration was noticed in the course of time, but a precipitate of sulfid of lead failed to appear even after the solution had stood for several days.

This experiment was repeated a number of times with the same result, giving thus the assurance that the error due to the excessively slight solubility of the oxalate of lead, under conditions formulated, would not act as a disqualification of a technical method which was based on its use.

The oxalate of lead precipitated from cold alcoholic solutions comes down as a heavy white flocculent precipitate, which settles quickly on agitating the solution either by stirring or shaking, leaving the supernatant liquid perfectly clear. From heated solutions the precipitate falls as a brilliant crystalline powder. The composition of the salt is, however, in both cases the same, its formula being PbC_2O_4, containing 70.18 per cent. of lead.

The crystalline precipitate filters rapidly and is easily washed; the flocculent variety becomes reduced in bulk and crystalline on being washed with hot water. It is advisable to precipitate the oxalate from the solution which has been heated to 65° C.

Pure lead having been prepared by reduction from C. P. acetate of lead, freeing the regulus from mechanical impurities and rolling it into thin sheet lead, varying quantities were weighed out to determine the accuracy of the method under consideration.

The standard of the permanganate of potassium solution containing 1.58 grams of $KMnO_4$ to the liter was established as follows: 3.65 grams C. P. crystallized oxalic acid were dissolved in 500 cc. distilled water, from which three separate portions of twenty-five cc. each were taken, five cc. concentrated sulfuric acid added, and the titration performed with the previously prepared permanganate solution. There were used in:

Experiment.	Oxalic acid, cc.	Cryst. oxalic acid, gm.	$KMnO_4$, cc.
1	25	0.1825	58.30
2	25	0.1825	58.35
3	25	0.1825	58.40

Making an average of 58.35 cc. of permanganate solution used, or one cc. $KMnO_4$ solution = 0.003127 gram $C_2H_2O_4 \cdot 2H_2O$ from which by the simple stoichometrical calculation one cc. $KMnO_4$ solution = 0.00513 gram lead, in the form of oxalate.

The standard being established, a portion of lead was weighed out and dissolved in three cc. concentrated nitric acid, diluted with ten cc. hot water and carbonate of sodium in slight excess added. The precipitate was dissolved by the addition of five cc. strong acetic acid, twenty cc. of ninety-five per cent alcohol being then added to the solution. This was heated to 65° C. and the lead precipitated by adding ten cc. of a saturated solution of oxalic acid, the precipitate, after settling, being filtered and thoroughly washed with hot water. The lead oxalate was now rinsed from the filter into a beaker, fifty cc. hot water and five cc. concentrated sulfuric acid added. The solution was warmed to about 65° C. and the titration on the freed oxalic acid effected. Ten determinations were made, the results being

Exp. No.	Weight of lead taken gm.	$KMnO_4$ used cc.	Weight of lead found	Per cent obtained
4	0.05302	10.4	0.05335	[illegible]
5	0.10150	19.7	0.10106	[illegible]
6	0.15266	29.7	0.15236	[illegible]
7	0.20878	40.6	0.20827	[illegible]
8	0.25540	49.7	0.25496	[illegible]
9	0.30016	58.5	0.29916	[illegible]
10	0.35204	68.6	0.35191	[illegible]
11	0.40200	78.4	0.40210	[illegible]
12	0.45252	88.2	0.45236	[illegible]
13	0.49876	97.1	0.49812	[illegible]

The average percentage obtained being [illegible]

In order to establish comparisons on a basis which would be of greater value, in that the determinations would be made under conditions necessary in the carrying out of the method on ores and metallurgical products, another series of experiments was instituted, the lead taken for the analysis being brought into the solution, and reconverted into metallic lead, from which point on the process was as above described.

The precipitate of metallic lead from hydrochloric acid solutions was found to be easily, as well as completely effected by

means of pure granulated zinc, the article used having been made by Merk, the granules being of a diameter small enough to allow them to pass through a screen containing thirty meshes to the linear inch. Investigation proved it to be free from lead.

Dilute hydrochloric acid has no action whatever on metallic lead, and even boiling concentrated hydrochloric acid scarcely attacks it. From dilute solutions of pure sulfate of lead in hydrochloric acid granulated zinc precipitates the lead quickly as a sponge, which is easily washed.

The lead taken for the following experiments was dissolved in five cc. concentrated nitric acid, ten cc. concentrated sulfuric acid added, and evaporated until the sulfuric acid fumes appeared. To the mass, when cool, water was added and the sulfate of lead filtered off, washed first with hot water acidified with sulfuric acid, and finally with hot water alone. The sulfate of lead was then rinsed off the filter into a beaker, three cc. concentrated hydrochloric acid added, and enough water to bring the bulk to about 100 cc. The solution was boiled until the whole of the sulfate of lead was dissolved and two grams of pure granulated zinc added. After an action of five minutes, an additional 0.50 gram of zinc was introduced and the solution again brought to the boiling point when ten cc. more of concentrated hydrochloric acid were added. In a few minutes all of the zinc had dissolved. The solution was decanted from the lead sponge, the latter washed, re-dissolved in nitric acid and the precipitation as oxalate made as before described. The results were:

Exp. No.	Weight of lead taken, gm.	$KMnO_4$ used, cc.	Weight of lead found.	Per cent. obtained.
14	0.22150	42.9	0.22007	99.76
15	0.21134	40.9	0.20981	99.32
16	0.20756	40.2	0.20632	99.39
17	0.16683	32.5	0.16672	99.94

The average percentage obtained being 99.60.

It has been mentioned that when pure sulfate of lead in hydrochloric acid solutions is precipitated with granulated zinc it comes down in a coherent, spongy mass. This is, however, not the case when certain impurities are associated with the precipitate, notably bismuth, a not uncommon constituent of our Western ores.

When the sulfate of lead is impure, the precipitated lead comes down in separate pieces which are with difficulty made to cohere or the complete precipitation may even be prevented. The presence of bismuth especially is likely to prove vexatious and vitiate correct results if proper precautions for its total elimination from the sulfate of lead are not taken. The deportment of bismuth in solutions is so interesting that a mention of its behavior where it exists as sulfate, may be of interest.

L. Laurent observes that there exist two sulfates of bismuth the one soluble and the other insoluble in water. If bismuth be dissolved in boiling nitric acid and sulfuric acid added to the solution, there is at times an abundant precipitate produced and at others none whatever. The precipitate may be easily soluble in small quantities of water and again remain entirely insoluble no matter how large an amount of water be used. These phenomena are dependent upon the relative amounts of free sulfuric acid present when the sulfate of bismuth is formed, and the temperature of the solution. If sulfuric acid be added to a cold solution of nitrate of bismuth, care being taken to prevent the mixture from becoming heated, no precipitate will be produced. If an excess of sulfuric acid should have been added, a sulfate of bismuth will be deposited in crystalline needles, which is scarcely soluble in sulfuric acid, but extremely so in water. If, however, a solution of this salt be heated, whether the quantity of water be large or small, a sulfate of bismuth will again be *gradually* precipitated which is insoluble in either hot or cold water, even if a considerable quantity of sulfuric acid should have been added.

I have found that the difficulty in regard to effecting a complete solution of bismuth may be obviated if, in the treatment of ores and metallurgical products, a large excess of sulfuric acid is added to the nitric acid solution, so that when the evaporation takes place and the sulfuric acid fumes appear the mass will still be in a fluid and not in a pasty condition. If the mixture is then allowed to cool, and cold water added gradually to prevent heating, all of the bismuth goes into solution and remains so for a sufficient length of time to allow a filtration and separation from the sulfate of lead to be effected.

Another impurity not unlikely to contaminate the sulfate of

lead, if sufficient excess of sulfuric acid is not added, is antimony. Such antimony would also be reduced to the metallic state in conjunction with the lead by the zinc. However, in re-effecting the solution of the lead by nitric acid, the antimony would remain as the insoluble oxid and thus be eliminated.

The following experiments demonstrate that even considerable quantities of bismuth and antimony, when originally present, do not essentially effect the accuracy of the process. Five portions of lead were weighed out, and to these, severally, 100 milligrams each of metallic antimony and bismuth were added:

Exp. No.	Weight of lead taken, mgms.	$KMnO_4$ used, cc.	Weight of lead found.	Percentage. obtained.
18	215.44	41.9	214.94	99.76
19	232.21	45.1	231.36	99.63
20	258.58	50.1	257.01	99.38
21	244.50	47.6	244.18	99.86
22	250.74	48.5	248.80	99.22

The average percentage obtained being 99.57.

In ordinary practice such combinations as given in the experiments just noted are hardly likely to be met with, and the results obtained are an ample demonstration of the sufficient accuracy of the method for all technical purposes.

In the analysis of ores and furnace products the following plan of operation has been found most suitable:

Place one gram or 0.50 gram, according to richness of the material, in a four inch casserole; add fifteen cc. concentrated nitric acid and fifteen cc. concentrated sulfuric acid; cover with watch glass and heat on a hot plate until the decomposition is effected, and the fumes of sulfuric acid appear. Remove and cool; when cool, gradually add about fifty cc. of cold water, heat to boiling and immediately filter. Wash well with boiling water slightly acidified with sulfuric acid, and finally with plain hot water. Now rinse the insoluble residue into a beaker of about 200 cc. capacity, using not more than fifty cc. water; add five cc. concentrated hydrochloric acid, cover with watch glass and boil briskly for five minutes. The sulfates of lead and lime pass into solution.

If much silica and sulfate of barium be present, it is well to filter and wash well with boiling water. If such filtration is

undertaken, it must be done rapidly. Small amounts of silica do not interfere, but larger quantities prevent the subsequent precipitation of the lead in one spongy mass.

Dilute the solution with water to about 100 cc., keeping it hot but not boiling. Now add two grams of granulated zinc. The lead begins immediately to be deposited as a metallic sponge. When the action of the acid on the zinc has apparently ceased add an additional 0.50 gram. After five minutes the solution is again boiled for a few minutes and then ten cc. concentrated hydrochloric acid added. This dissolves the remainder of the zinc very quickly, and when the reaction is completed the lead sponge will be found floating on the surface of the liquid. Decant solution, wash the lead sponge with cold water, and press it out flat with the finger. Dissolve it in one cc. concentrated nitric acid and twenty cc. hot water. Add now a slight excess of carbonate of sodium (the salt is preferable to the solution), and redissolve the precipitated carbonate of lead by adding five cc. strong acetic acid; add twenty cc. of ninety-five per cent. alcohol, heat the solution to 65° C. and precipitate the lead with a saturated solution of pure crystallized oxalic acid. The lead comes down at once as a dense white crystalline precipitate. Stir briskly and the precipitate settles rapidly, leaving a perfectly clear supernatant liquid. Filter and wash precipitate three times with a hot mixture of alcohol and water (1:1), and then four times with hot water alone. (In washing the precipitate it is well to use a fine jet, keeping the stream on the filter and not allowing it to flow on the glass, as otherwise the precipitate is apt to creep upon the funnel, and thus occasion loss.) When thoroughly washed, the precipitate is rinsed into a flask or beaker with about fifty cc. hot water, five cc. concentrated sulfuric acid added and the oxalic acid determined by permanganate of potassium solution in the usual way.

The only precautions to be observed are those which have already been mentioned with reference to bismuth and when large amounts of silica or sulfate of barium are present.

As the ratio of the atomic weight of lead to that of the combined oxalic acid is very high, any error occurring in the titration will be magnified. It is advisable therefore, to use quite dilute

solutions of permanganate of potassium, the strength of this being not greater than 1.58 grams $KMnO_4$ to one liter, which will give a strength of solution, one cc. equals about fifty milligrams of lead.

The standard of the solution in terms of lead is obtained by multiplying the standard in terms of crystallized oxalic acid by 1.6428.

The time involved in the execution of the method on a single assay occupies from thirty-five to forty minutes, and the carrying out of a number of assays simultaneously is easily feasible.

The following results indicate what concordance can be obtained by the method:

Exp. No.		Per cent.
23	Broken Hill ore	27.61—27.50
24	Silver precipitate of leaching process	28.86—28.75
25	Oxidized ore	2.56— 2.66
26	Galena associated with pyrite and chalcopyrite	22.25—21.95
27	Galena ore (gravimetric, 66.75 per cent. lead)	66.58—66.66
28	Oxidized ore	41.04—41.29

THE ANALYSIS OF A SCALE FORMED IN THE PROCESS OF MANUFACTURING BICARBONATE OF SODA BY THE AMMONIA-SODA PROCESS.

By J. D. Pennock, Solvay Process Company, Syracuse, N. Y.

In 1886 I sent a sample of the scale which we have to contend with in the ammonia-soda manufacture to Professor Cooke of Harvard College. This scale was formed on the inside of a pipe conveying an ammoniated and partially carbonated brine. The scale varies in thickness from one-half to two inches. This particular piece of scale was given to one of the Professor's pupils, Mr. Geo. W. Leighton, who made an examination of it.

The results, which correspond closely to my own, may be found in the *Proceedings of the American Academy of Arts and Sciences*, 1886, 159. He says: "The scale is semi-transparent with a vitreous luster and of greenish gray color, although sometimes black on the surface; usually covered with crystalline planes, which have at first sight the appearance of octahedral forms projecting from the surface, but on closer examination

were found to be the terminations of prisms extending down into the body of the scale." The result of his analysis was

Substance estimated.	Number of Analysis							
	1	2	3	4	5	6	7	8
H_2O at 100° C.					0.31	0.30	[illegible]	
H_2O at 230° C.	0.63	0.63						
CaO			2.08	1.99	[illegible]	[illegible]	[illegible]	
FeO	0.054	0.045						
MgO			14.90	14.[illegible]		[illegible]	[illegible]	
Na_2O	38.71		38.45	38.[illegible]				
Cl	11.45		11.[illegible]	11.45				
CO_2	36.24			35.[illegible]	35.[illegible]	[illegible]		[illegible]

Taking now the means of these determinations and assuming that the chlorin is combined with sodium, while the carbon dioxid is distributed among the rest of the base we obtain as the final average result of the analysis:

	Found	Theory
NaCl	22.[illegible]	22.[illegible]
Na_2CO_3	40.62	[illegible]
$MgCO_3$	31.56	[illegible]
$CaCO_3$	3.55	
$FeCO_3$	0.08	
H_2O	0.63	
CO_2 in excess	0.64	

It will be seen that this scale very closely approximates a salt represented by the formula $MgCO_3.Na_2CO_3.NaCl$.

I have recently examined another scale taken from an evaporating apparatus through which the same ammoniated and carbonated brine was passing, but at a somewhat lower temperature. This scale is not so thick as the other, is white and semi-transparent, and the crystals, though definitely formed, are microscopic. It is entirely, or nearly, free from salt, thus differing from the previously mentioned scale, and evidently is the union of one molecule of Na_2CO_3 with one of $MgCO_3$. The scale is three-quarters of an inch thick, was four months forming, and is thrown out from a solution which contains only a slight percentage of magnesium impurity.

The original brine is of the following composition:

$CaSO_4$	4.54	grams per liter.
$CaCl_2$	2.14	" "
$MgCl_2$	0.586	" "
NaCl	290.00	" "

Of course, the action of the ammonia and carbonic acid is that of purifying the brine from lime and magnesia, and as a result the ammoniated brine passing through the apparatus (in volume about 500 cubic meters per twenty-four hours) where the scale is formed contains the following percentage of $MgCl_2$, obtained from analyses of the liquor on different days:

	1	2	3	4	5	6
$MgCl_2$, grams per liter,	0.076	0.123	0.046	0.054	0.092	0.068

The following are the results of analyses of two samples taken from different parts of a large piece of the scale. If the liquor is not well settled, a little $CaCO_3$ goes along with the liquor in suspension and is held by the double salt in crystallization.

	Per Cent.	
	No. 1, dry.	No. 2.
Silica	0.10	0.17
Fe_2O_3, Al_2O_3	0.11	0.07
CaO	1.54	1.20
MgO	19.04	18.74
Na_2O	34.22	33.29
CO_2	45.30	45.20
Cl	0.24	0.14
Loss at 100°	——	1.12

The combination of the above is probably thus:

	No. 1.	No. 2.
Silica	0.10	0.17
$FeCO_3$	0.15	0.10
$CaCO_3$	2.75	2.14
$MgCO_3$	39.98	39.35
Na_2CO_3	58.50	57.21
NaCl	0.40	0.32
Loss at 100° C.	——	1.12

The composition of this scale approximates sufficiently close to that of the crystalline substance containing one molecule of Na_2CO_3 and one molecule of $MgCO_3$ to say that it is the double salt, $Na_2CO_3, MgCO_3$.

The other constituents are the suspended impurities in the liquor from which the scale is formed.

This scale, which is a salt formed by one molecule of Na_2CO_3 and one molecule of $MgCO_3$, is formed from the same liquor that throws out the other scale consisting of one molecule each of Na_2CO_3, $MgCO_3$ and NaCl, though the temperature in the first case is somewhat lower.

Hydrochloric acid was added to two grams of the scale from which analysis No. 2 was made. The solution of the chlorids was evaporated to dryness and heated in a hot air bath at [illegible] C to constant weight.

This weight corresponds closely to the theoretical weight calculated from the percentages of the constituents according to analysis No. 2.

	Grams
Silica	0.0034
Fe_2Cl_6	0.0028
$CaCl_2$	0.0075
$MgCl_2$	0.[illegible]
NaCl	1.[illegible]
Total	2.[illegible]
Weight of chlorids dried	2.22[illegible]

According to *Watts' Dictionary*, 1, 788, the double salt $MgCO_3 \cdot Na_2CO_3$ is obtained in anhydrous microscopic crystals by digesting magnesia alba for twelve or fifteen hours at [illegible] or [illegible] C with diacid carbonate of sodium.

"The carbonate of magnesia and of soda is rapidly decomposed by water." (Deville, *Ann. chim. phys.* [3] **33**, [illegible]) I did not find this to be the case with the substance under consideration. Four lots of five grams each of the finely ground scale were put in beakers with 100 cc of distilled water.

No. 1 was kept at 20 C for half an hour. No. 2 was kept at 50 C for half an hour. No. 3 was kept at 75 C for half an hour. No. 4 was boiled for half an hour adding water to maintain the same volume. Each was then filtered and washed with alcohol. The filtrates were analyzed for Na_2CO_3 and $MgCO_3$ with the following results:

	Grams Na_2CO_3	Grams $MgCO_3$
No. 1 filtrate contained	[illegible]	[illegible]
" 2 "	[illegible]	[illegible]
" 3 "	[illegible]	[illegible]
" 4 "	[illegible]	[illegible]

Percentage of the scale soluble in 100 cc. of water:

	Per Cent.
No. 1, at 20° C.,	2.82
" 2, " 50° C.,	3.05
" 3, " 75° C.,	3.05
" 4, boiling,	3.60

THE DETERMINATION OF PHOSPHORIC ACID IN BASIC SLAGS.*

By Dr. Adolf F. Jolles.

The views on the solvent in the determination of phosphoric acid in basic slags differ widely from each other. We may particularize two directions, one of which recommends the samples to be opened up with concentrated sulfuric acid and the other with hydrochloric acid.

At a meeting of Austrian managers and officials of agricultural experimental stations, held at Vienna on August 30, 1890, Dr. von Lorenz recommended the use of Maercker's process exactly as it had been proposed at Bonn Congress of the Experimental Stations in 1889. I have had repeated opportunity to analyze basic slags both by molybdenum method and by Maercker's process, and I always obtained differences in the percentage of phosphoric acid which were proportional to the percentage of lime. These differences are to be referred to the well-known fact that the gypsum liberated on opening up the slags with concentrated sulfuric acid incloses particles of calcium phosphate which are thus withdrawn from the solution. I have found similar losses of phosphoric acid when using hydrochloric acid.

Last year H. and E. Albert, of Biebrich, on the basis of numerous experiments, have recommended the following method for determining total phosphoric acid in basic slags, and have introduced it into the laboratory of their works:

Five gms. of finely-ground slag are moistened with a little water in a flask of the capacity of 500 cc. and boiled upon the sand bath with 40 cc. of hydrochloric at 16°–20° Bé. The mixture is boiled until there remain only a few cc. of a thick paste of silicic jelly, allowed to cool, and a little water is added. It is

* Chem. News, Nov. 25, 1892, from Ztschr. anal. Chem.

then shaken until the thick clots of silicic acid are very finely divided, made up to 500 cc. with water, and filtered. The [illegible] cc. of the filtrate are mixed with 15 cc. of Joulie's solution ([illegible] gms. citric acid made up to one liter with ammonia of specific gravity 0.9), and then precipitated in the ordinary manner with magnesia mixture, ignited, and weighed. There is no danger of obtaining silica in the magnesia precipitate, since many experiments have proved that the condensation of the hydrochloric solution to a thick jelly is sufficient to render the silica insoluble. If a standard solution of uranium is at hand we dissolve (if the presence of silica is suspected) the moist precipitate on the filter in a little nitric acid, and titrate in the usual manner.

I have had this process and, as a check, the molybdenum method carried out in numerous analyses of basic slags in my laboratory, with the result that the Albert method, both gravimetrically and volumetrically, yielded far too high results in comparison with the molybdenum method. The cause of these discrepancies can only be sought for in the imperfect elimination of the silica.

I cannot in my analyses confirm the above quoted statement of H. and E. Albert, since I have always been able to recognize the presence of silica in the precipitates of magnesia. I have then, dissolved the magnesia precipitate in hydrochloric acid, evaporated it to dryness, heated the residue to 120° in the air bath, re-dissolved in hydrochloric acid, and weighed the silica.

The differences varied according to the time of boiling and I obtained results agreeing with those of the molybdenum method only on boiling the basic slag meal in hydrochloric acid, evaporating completely to dryness, and heating in the air bath to [illegible]. This method may thus be modified by evaporating the silica to perfect dryness, retaining the further course of the analysis.

As for the volumetric determination, I have dissolved the moist precipitate of ammonium magnesium phosphate in a little nitric acid, neutralized it with ammonia, dissolved it in acetic acid and titrated with solution of uranium. The results obtained have, by accident, coincided with the gravimetric results according to Albert, so that I at first believed that no silica was present in the precipitate of ammonium magnesium. In fact however

I found in every precipitate ponderable quantities of silica; therefore, according to the check titration with uranium solution I should have obtained less phosphoric acid than by weighing, which was not the case. There occur here also sources of error which act in opposite directions and which may even mutually compensate each other.

The most important defect of this method lies in the untrustworthiness of the indicator. I have frequently observed that the brown color does not appear at once, but not until the lapse of some minutes.

I believe that in the analysis of manures the motion accepted at the Congress of Chemists at Hanover in 1889 ought to be kept in mind, according to which "the volumetric determination of phosphoric acid is regarded as no longer adequate to the demands of the age and is declared untrustworthy."

For the volumetric determination of phosphoric acid in basic slag, I venture to propose the following modification of the method of H. and E. Albert:

Five gms. of fine slag-meal is moistened with a little water in a capsule, boiled with 40 cc. of hydrochloric acid at about 20° Bé., and evaporated to perfect dryness. The residue is heated to 120° in the air bath, moistened with hydrochloric acid when cold, taken up in water, and filtered. The filtrate is made up to 500 cc., 50 cc. of which are mixed with citrate solution, and the phosphoric acid is precipitated in the ordinary manner with magnesia mixture, when the precipitate is dried, ignited, and weighed.

With this procedure I have obtained results which agreed fairly with those of the molybdenum method. In cases where the analyst wishes to check himself or other chemists, and in disputed cases, the molybdenum method is exclusively admissible.

A METHOD FOR THE QUANTITATIVE SEPARATION OF BARIUM FROM STRONTIUM BY THE ACTION OF AMYL ALCOHOL ON THE BROMIDS.*

BY PHILIP E. BROWNING.

The existing methods upon which dependence can be made in the separation of barium from strontium are few in number.

*AM. J. SCI., 44, 459.

Dr. R. Fresenius in discussing them through several numbers of his journal* concludes that the only one which gives perfectly reliable results consists of the precipitation of the barium by a double treatment with ammonium chromate in acetic acid solution. Having demonstrated the possibility of separating both barium and strontium from calcium by the dehydrating and appropriate solvent action of boiling amyl alcohol on the nitrates† the possibility of a similar method of separation by the use of suitable salts of barium and strontium seemed worthy of investigation and necessary to complete the series as applied to this group. In looking about for suitable salts upon which to experiment the behavior of the chlorids was suggestive. Barium chlorid is completely insoluble in amyl alcohol while the corresponding strontium salt is somewhat soluble. The possibility of finding strontium bromid more readily soluble than the corresponding chlorid seemed worthy of attention. The method of preparation followed was the treatment of the precipitated and thoroughly washed carbonates of barium and strontium with hydrobromic acid prepared‡ by mixing definite proportions of potassium bromid in solutions with sulfuric acid and water while hot, filtering off the potassium sulfate which separates on cooling and redistilling the filtrate until the distillate contains no appreciable trace of sulfuric acid. The standards of the solutions of barium and strontium bromids made in this way were determined by precipitating definite portions, measured and weighed with sulfuric acid, the strontium after the accepted method of adding ethyl alcohol to increase the insolubility and the barium after the manner suggested by Dr. F. W. Mar‡ precipitating with an excess of sulfuric acid in the presence of hydrochloric acid. The mean of closely agreeing results was taken as the standard. Preliminary experiments on the bromids formed in this way gave encouraging results, the barium salt appearing to be almost completely insoluble while the strontium salt dissolved freely. The first series of experiments were directed toward a quantitative determination of the solubility of barium bromid in the alcohol

* [illegible]

† [illegible]

‡ [illegible]

§ [illegible]

Definite portions of the standarized solution of barium bromid were measured from a burette into counterpoised beakers of about fifty cc. capacity and weighed as a check on the burette reading. This solution was then evaporated to dryness, and the residue was dissolved in a few drops of water and boiled with ten cc. of amyl alcohol. The separating bromid was filtered off on an asbestos felt contained in a perforated platinum crucible, the whole having been previously ignited and weighed. The crucible containing the bromid was at first dried at 140°–150° C. in an air bath after the manner described in the previous papers, and weighed. The unsuccessful attempt to get a constant weight, however, proved the impossibility of weighing as bromid, the weight decreasing rapidly with each successive drying. It was deemed best, accordingly, to dissolve the bromid from the felt into a beaker placed to receive it, and to precipitate with sulfuric acid in the presence of hydrochloric acid, after the same manner followed in the determinations of the standards. The precipitated sulfate, which in a few minutes settles completely, was filtered off upon the same felt from which the bromid had been dissolved, dried, ignited to low redness, and weighed. Series I gives the results of several experiments made after this manner which show the solubility of the barium salt to be about 0.0013 gms. on the oxid in ten cc. of amyl alcohol. The filtrate after boillng with amyl alcohol was evaporated and the residue was treated with sulfuric acid and weighed; or the filtrate was precipitated directly by adding sulfuric acid, enough ethyl alcohol being added to secure thorough mixture. The amount of sulfate found agreed uniformly with the loss determined in the residue after boiling. A portion of the salt which dissolved in the alcohol on being examined before the spectroscope gave only the green bands characteristic of barium.

SERIES I.

	BaO taken, gm.	BaO found, gm.	Error, gm.
1	0.1234	0.1222	0.0012—
2	0.0824	0.0809	0.0015—
3	0.0823	0.0809	0.0014—
4	0.0818	0.0803	0.0015—
5	0.0733	0.0720	0.0013—

Several methods of treatment were followed to prevent [illegible] possible, this solubility, such as the addition of a few drops of hydrobromic acid before boiling, of the same after the barium bromid had separated, of a few drops of ethylene dibromid or ethyl bromid at the completion of the boiling, of a few drops of bromin water before boiling, etc. The results of these experiments showed these modifications to be of little or no value.

On boiling the strontium bromid with the alcohol slight specks separated occasionally, which, on the addition of a drop of hydrobromic acid, went into solution and did not appear on re-boiling. In order to determine the solubility of the strontium bromid in the alcohol a saturated solution was obtained by boiling an excess of the strontium salt with the alcohol, the salt in a measured portion of ten cc. was precipitated as sulfate by the addition of ethyl alcohol, and sulfuric acid, and weighed. Duplicate determination showed the solubility to be about 0.2 gm. on the oxid in ten cc. of the alcohol. The mode of procedure for the separation of these elements was identical with that already described in the case of barium alone up to the point at which the barium was filtered off, except, of course, the addition at first of a measured and weighed amount of a previously standardized solution of strontium bromid. The strontium was precipitated from the filtrate as sulfate by dilute sulfuric acid, ethyl alcohol being added to secure thorough mixture. These precipitates were generally filtered off upon asbestos felts, and although their gelatinous character delayed the filtration somewhat, the drying and burning of a filter paper with the possible danger of loss by reduction in the presence of burning paper was avoided. Series II gives the results of a single treatment, and it will be seen that there is apparently a slight contamination of the barium by the strontium which, where the latter is present in large quantities, balances the solubility of the barium [illegible] in the oxid). Where the amounts of strontium taken are small the loss of barium due to solubility appears.

SERIES II.

	BaO taken, gm.	Ba found, gm.	Error, gm.	SrO taken, gm.	SrO found, gm.	Error, gm.
1	0.1228	0.1225	0.0003—	0.1070	0.1065	0.0005—
2	0.1227	0.1231	0.0004+	0.1074	0.1069	0.0005—
3	0.1224	0.1228	0.0004+	0.1070	0.1067	0.0003—
4	0.1217	0.1201	0.0016—	0.0364	0.0372	0.0008+
5	0.1216	0.1222	0.0006+	0.0133	0.1124	0.0009—
6	0.0974	0.0970	0.0004—	0.0719	0.0721	0.0002+
7	0.0971	0.0973	0.0002+	0.0730	0.0727	0.0003—
8	0.0970	0.0971	0.0001+	0.0718	0.0716	0.0002—
9	0.0411	0.0390	0.0021—	0.0365	0.0385	0.0020+
10	0.0243	0.0234	0.0009—	0.1072	0.1072	0.0000

Series III gives the result of a double treatment. In this series the contaminating effect of the strontium salt disappears almost entirely, leaving a deficiency of about 0.0025 gm. on the oxid to be added to the barium, and a corresponding amount of sulfate (0.0040 gm.) to be subtracted from the strontium sulfate before calculating it to the condition of the oxid. The manipulation is the same as that outlined for the single treatment, as far as the completion of the first boiling. At this point the amyl alcohol containing most of the strontium in solution was decanted upon a weighed and ignited felt and collected in a beaker placed to receive it. The residue of barium with traces of strontium was then dissolved in a few drops of water, a drop of hydrobromic acid was added and the boiling was repeated with another portion of ten cc. of amyl alcohol. Upon reaching the boiling point of the alcohol the beaker was removed, and the barium salt was filtered upon the felt through which the first portion had been decanted, and treated as before described.

SERIES III.

	BaO taken, gm.	(Corrected). BaO found, gm.	Error, gm.	SrO taken, gm.	(Corrected). SrO found, gm.	Error, gm.
1	0.1212	0.1219	0.0007+	0.1068	0.1071	0.0003+
2	0.1215	0.1219	0.0004+	0.0358	0.0359	0.0001+
3	0.1220	0.1221	0.0001+	0.0353	0.0347	0.0006—
4	0.1212	0.1220	0.0008+	0.0363	0.0358	0.0005—
5	0.1219	0.1221	0.0002+	0.0361	0.0354	0.0007—
6	0.1211	0.1218	0.0007+	0.1126	0.1116	0.0010—
7	0.1319	0.1319	0.0000	0.0577	0.0586	0.0009+
8	0.0496	0.0492	0.0004—	0.0574	0.0579	0.0005+

The method is rapid, and while the correction to be applied owing to the solubility of the barium salt is large it is so definite that it cannot be objectionable. The author in conclusion would express his indebtedness to Professor F. A. Gooch of the Kent Laboratory for the many helpful suggestions received from him bearing upon this investigation.

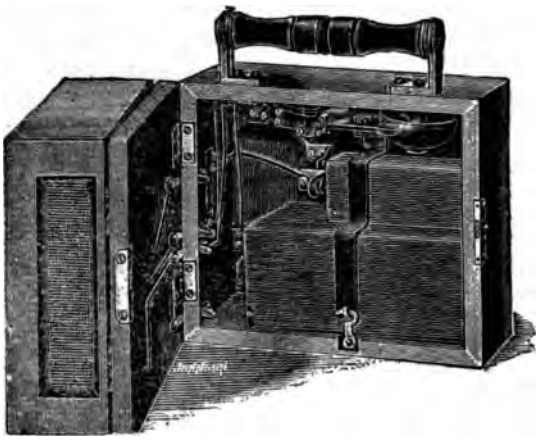
MURDAY'S FIRE-DAMP DETECTOR *

The instrument here illustrated is intended for estimating extremely small percentages of fire-damp in the air of coal mines and is much more sensitive than any other apparatus of the kind in the market. It will indicate the presence of less than [illegible] per cent. of fire-damp or about the one-hundredth part of the amount necessary for an explosion. The principle on which it works, however, is the same as has been applied before for the same purpose. There are two platinum wires, one in a sealed chamber

and the other in a cage of wire gauze through which the air of the mine penetrates. Equal electric currents from a dry battery pass through these wires, and heat them up to a certain necessary temperature. When there is no fire damp in the air the galvanometer needle points to zero. When however fire damp comes in the platinum wire in the gauze chamber commences to glow according to the well known property of the metal

* Engineering and Mining Journal.

This glowing causes a variation in the current which passes along the wire, and this variation is indicated by the galvanometer



needle. The amount of glow depends directly on the percentage of fire-damp present, and thus the deflection of the galvanometer needle indicates accurately the amount of gas present in the air. An alarm bell can be adjusted in such a way that when a certain percentage is reached, it is automatically rung. When the apparatus is not in use, the tension of the springs in the indicating mechanism is taken off by pressing a knob in order that the life of the apparatus shall be prolonged as much as possible. It will be seen that the apparatus is automatic and the readings are direct.

CONCERNING THE CONSTANT TO BE USED IN CLERGET'S INVERSION PROCESS.

To the Editor of The Journal of Analytical and Applied Chemistry:

Mr. Theodor Breyer, in the September number of your Journal, continues to insist that the inversion tests reported by myself and others some years since were conducted in accordance with Clerget's *original* method, notwithstanding my statement to the contrary in the August issue.

He goes still further and intimates that I, in my previous

communication, made a deliberate misstatement as to the manner in which those experiments were carried out, quoting in support of his assertion from that part of the report with reference to this subject which appeared in certain publications soon after the issuance of the pamphlet previously referred to.

This portion of the report to which I allude was prepared for publication along with the methods of analysis of the Sugar Chemists' Association, the whole matter being issued in a single pamphlet.

On page 207 of this pamphlet the process of inversion employed (the same as that given by Tucker) was described in these words—"the solution is heated in a water bath at 68°-75° C. for a period of fifteen minutes." It was also recommended, as stated in my previous communication, that in "calculating the true per cent. of sucrose from the data thus obtained (*i. e.* by the use of the method given) instead of Clerget's original constant of 144, the revised figure of 142.4 should be used."

In view of the fact that the methods employed by the Sugar Chemists' Association were referred to in the first part of our report as being the methods it was designed to test, it was not presumed that any one would suppose that Clerget's original unmodified method was followed in all its details, especially since reference was made to the method previously described, only one method of inversion being described in detail in the pamphlet.

It was certainly no more my intention to convey the idea that the Clerget original process was used than it was the intention of Mr. Breyer to produce the impression that Clerget's original formula "is used by all the chemists in the sugar industry," yet one might draw such conclusion, if as strict an interpretation were placed upon his words as he has placed upon certain isolated sentences of my report.

Numbers of authors refer to various modifications of the of the original inversion process as "Clerget's Method of Inversion," and yet from this designation one does not necessarily infer that the unmodified method is alluded to.

It is frequently the case, too, that European chemists in reporting results give "sucrose according to Clerget" where the Herzfeld process or other modification has been employed.

The official inversion method of the French Sugar Chemists' Association differs somewhat appreciably from that of Clerget and yet it is designated "Clerget's Inversion Process." While it might be possible for one to draw the inference that the original method of Clerget was employed in the inversion tests by reading isolated excerpts from the pamphlet alluded to, yet no one could legitimately reach such a conclusion after a careful perusal of the *full* report as originally published.

However, in further support of my statement, I will quote from the proceedings of a meeting of the Louisiana Sugar Chemists' Association, as reported in *The Louisiana Planter* and published long in advance of the appearance of Mr. Breyer's letter.

In giving some results of further experiments in inversion tests, I stated "that it is intended to carry the investigations still further, using Clerget's *original* method of inversion instead of the one now generally used."

At a meeting a few weeks later, I stated (as reported in *The Louisiana Planter*), in making a report of some more recent results, that the "original experiments of the committee were not made specifically to test the correctness of the original figures of Clerget, but to determine what constant should be employed when the method in general use at that time was followed, this process being given in the methods of analysis of this association, and being the same as that described by Tucker." I also gave results corroborating those previously obtained, and, in addition, reported other experiments indicating "the correctness of Clerget's original figures, where Clerget's *own* method is followed closely."

Mr. Breyer quotes from the methods of analysis of the Association of Official Agricultural Chemists for 1891 in controversion of my explanation as to the omission of essential changes in the conditions of the inversion process at the time the constant was changed, but this is no refutation of my statement, as this omission would not have occurred, had it not been for the inadvertence referred to.

Mr. Breyer also makes reference to certain methods of sugar analysis adopted by the Association of Official Agricultural Chemists in 1889, whereas, as a matter of fact, no methods of

sugar analysis were adopted that year. The methods of the Louisiana Sugar Chemists' Association were published in the report of 1889, but it was clearly stated by the secretary that no methods having been adopted by the Association, the Louisiana methods were inserted for provisional use.

With regard to the destruction of invert sugar by hydrochloric acid at temperatures above 70°, to which reference was made by Mr. Breyer, I would say that many authorities claim that a decomposition takes place at even lower temperatures. Ost (*Ztschr. f. des Vereins f. Rübenzuckerind.*, January, 1892) refers to this decomposition occurring even in the Herzfeld method of inversion, where a temperature of 70° is not exceeded and where the time of heating is only five minutes, so that it can not be claimed that a temperature of less than 70°, insures freedom from destruction of invert sugar.

Bornträger (*Scheibler's Neue Ztschr.*, 1892, **23**, 282) alludes to the danger of destruction of invert sugar by inversion by the processes ordinarily employed and recommends conducting inversion in the cold, using one-tenth volume of acid as usual.

There is still great lack of unanimity among chemists connected with the sugar industry, as to the exact value of the constant to be employed in inversion tests and also as to the best manner of execution of the inversion process.

Lacomble (*Bull. Assoc. chim. de Sucr. et Dist.*, **9**, 125) claims as the result of a large number of tests that a different constant should be employed in connection with different temperatures, a figure less than 144 being used where observations are made at low temperatures, while a larger number is suggested for temperatures above 20° C.

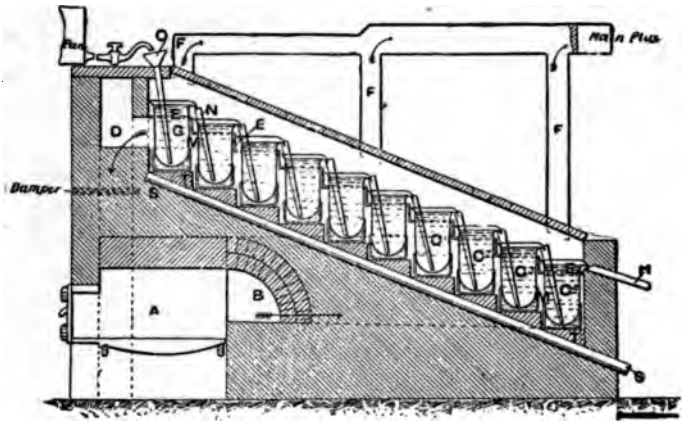
In conclusion, I would say that while I have recommended the use of a constant different from that of Clerget when the conditions of the inversion process itself were modified, I have never at any time claimed that a figure other than 144 should be employed where Clerget's original and unmodified method was followed. Mr. Breyer's assertions to the contrary notwithstanding,

B. B. Ross.

[illegible]

THE CONCENTRATION OF SULFURIC ACID IN GLASS VESSELS.*

With the present high price of platinum many attempts are being made in Europe to dispense with the platinum still which has been used for several years in concentrating sulfuric acid. Manufacturers appear to be going back to glass concentrators. This week *Industries* describes a new glass concentrator which is in use at Levinstein's chemical factory at Manchester, England. As will be seen in the accompanying illustration, ten glass vessels

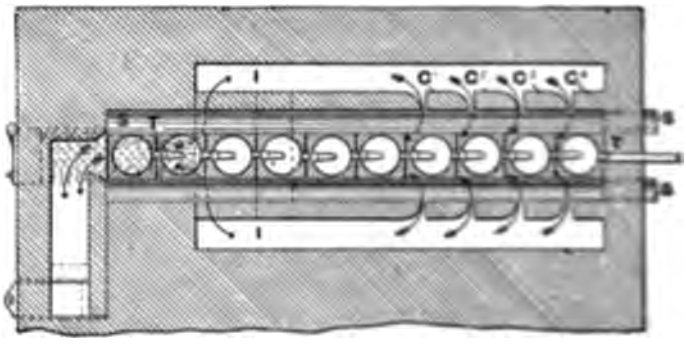


to each, ten inches diameter and twenty-one inches deep, are arranged on a terrace T of Stourbridge tiles. The steps are twenty-four inches long and twelve inches wide, and each step is five inches below the one above. The glasses rest on beds of clean sand in cast iron dishes. Each glass has a pouring spout which discharges into a funnel leading to the bottom of the glass below.

By this means the acid circulates throughout each glass and the concentration is thus made much more rapid and efficient. The heating gases from the furnace A pass along the side flues I and enter the terrace through the apertures C^1 C^2 C^3 C^4. The heating gases are prevented from approaching the surface of the acid in the glasses by the cast-iron terrace E. After circulating round the glasses they pass to the chimney through D. The fumes of concentration pass up the lead flues F to a coke column

* Engineering and Mining Journal.

for condensation. In case a glass breaks the gutter S at the side catches the spilled acid. The concentrated acid that comes away from the porcelain spout H at the bottom is led first to another series of glass coolers and afterwards to the usual lead coolers. The interposition of the glass coolers is arranged because it is found that sulfuric acid at a high temperature has an effect on lead. The output of a plant of this sort is thirty tons of acid



per week; the consumption of fuel is five tons of coke and two men are required to attend to it, one at night and one at day. The plant works with success and more will be built of the same pattern at Manchester.

NOTE ON THE METHOD FOR THE QUANTITATIVE SEPARATION OF STRONTIUM FROM CALCIUM BY THE ACTION OF AMYL ALCOHOL ON THE NITRATES.*

By Francis P. Treadwell.

Recent work on my method for the quantitative separation of strontium from calcium by the action of amyl alcohol on the nitrates† has demonstrated the possibility of using very much smaller amounts of amyl alcohol in the boiling than the amounts formerly used (thirty cc. for each treatment). By the use of smaller beakers (fifty cc. capacity) ten cc. of the alcohol may be conveniently substituted for thirty cc. and the correction for solubility of the strontium nitrate is thus reduced to a

* [illegible] 44 [illegible]
† [illegible] 42 [illegible]

0.001 gm. on the oxid to 0.0003 gm. in each treatment, and the corresponding amount of sulfate to be subtracted from the calcium sulfate before calculating to the condition of oxid is reduced from 0.0017 gm. to 0.0005 gm. in each treatment.

The necessity of a double treatment, or the use of two portions of ten cc. each of the alcohol, brings the total correction to 0.0006 gm. on the strontium oxid, and 0.0010 on the calcium as sulfate. For ordinary work such a correction may be disregarded. The following tables give the corrected and uncorrected results:

TABLE I (CORRECTION DISREGARDED).

	SrO taken, gm.	SrO found, gm.	Error, gm.	CaO taken, gm.	CaO found, gm.	Error, gm.
1	0.0570	0.0565	0.0005—	0.0534	0.0540	0.0006+
2	0.0273	0.0567	0.0006—	0.0534	0.0543	0.0009+
3	0.0585	0.0274	0.0011—	0.0272	0.0276	0.0004+
4	0.0568	0.0560	0.0008—	0.0535	0.0537	0.0002+
5	0.0568	0.0561	0.0007—	0.0533	0.0535	0.0002+
6	0.0288	0.0280	0.0008—	0.0271	0.0272	0.0001+
7	0.1420	0.1416	0.0004—	0.0535	0.0544	0.0009+
8	0.1419	0.1416	0.0003—	0.0665	0.0669	0.0004+
9	0.1135	0.1132	0.0003—	0.1066	0.1070	0.0004+
10	0.1137	0.1126	0.0011—	0.1064	0.1070	0.0006+

TABLE II (CORRECTION APPLIED).

	SrO taken, gm.	(Corrected). SrO found, gm.	Error, gm.	CaO taken, gm.	(Corrected). CaO found, gm.	Error, gm.
1	0.0570	0.0571	0.0001+	0.0534	0.0536	0.0002+
2	0.0573	0.0573	0.0000	0.0534	0.0539	0.0005+
3	0.0285	0.0280	0.0005—	0.0272	0.0272	0.0000
4	0.0568	0.0566	0.0002—	0.0535	0.0533	0.0002—
5	0.0568	0.0567	0.0001—	0.0533	0.0531	0.0002—
6	0.0288	0.0286	0.0002—	0.0271	0.0268	0.0003—
7	0.1420	0.1422	0.0002+	0.0535	0.0540	0.0005+
8	0.1419	0.1422	0.0003+	0.0665	0.0665	0.0000
9	0.1135	0.1138	0.0003+	0.1066	0.1066	0.0000
10	0.1137	0.1132	0.0005—	0.1064	0.1066	0.0002+

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Boron.—Atomic weight re-determined by W. Ramsay and Emily Aston. First, by dehydration of crystallized borax, with from five to ten grammes of the salt in each experiment. The

percentages of water found, and the corresponding atomic weights, were as follows:

Per cent H_2O	Atomic weight
47.1099	11.04
47.1433	10.97
47.2026	10.85
47.1912	10.87
47.1882	10.88
47.1865	10.885
47.1524	10.955
Mean.	10.921

Secondly, by distillation of *anhydrous* borax with methyl alcohol and hydrochloric acid. In this way the borax was converted into chloride, which was weighed.

Weight borax *	Weight NaCl *	Atomic weight
4.7684	2.7598	11.015
5.2740	3.0578	10.925
3.2344	1.8727	10.992
4.0862	2.3713	10.8[illegible]
3.4970	2.0266	10.9[illegible]
	Mean	10.952

* To the nearest tenth milligramme. In the original the weights are carried out to seven decimals.

In a second series of distillations the sodium chloride after weighing, was precipitated with silver nitrate. The silver chloride was then weighed on a Gooch filter, and its ratio to the original Na_2B_4O was thus ascertained. The results were as follows:

Weight Na_2B_4O	Weight NaCl	Atomic weight	Weight AgCl	Atomic weight
3.3115	3.0761	10.983	[illegible]	[illegible]
4.7840	2.7781	10.955	[illegible]	[illegible]
4.6617	2.8[illegible]	10.9[illegible]	[illegible]	[illegible]
1.7211	2.[illegible]	10.9[illegible]	[illegible]	[illegible]
3.3138	1.9187	10.9[illegible]	[illegible]	[illegible]
	Mean	10.966	Mean	[illegible]

The authors regard the second NaCl series as the best and adopt the value 10.966 for boron. The calculations were made with O = 16, H = 1.008, Na = 23.05, Cl = 35.45, and Ag = 107.[illegible]

—*Chem. News* 68, [illegible]

Gadolinium.—Determined by Bettendorff, by conversion of the oxide into sulphate.

1.0682 gm. Gd_2O_3 gave 1.7779 $Gd_2(SO_4)_3$
1.0580 " " " 1.7611 "
1.0796 " " " 1.7969 "

Hence, Gd = 156.33.

—*Ann. Chem.*, **270**, 376.

Palladium.—Keller and Smith, starting from carefully purified palladium, have re-determined its atomic weight by electrolysis of palladammonium chloride, $Pd(NH_3Cl)_2$. Two series of experiments gave as follows:

FIRST SERIES.

Weight $Pd(NH_3Cl)_2$, gms.	Weight Pd, gm.	Atomic weight.
1.29960	0.65630	106.928
1.05430	0.53253	106.918
1.92945	0.97455	106.915
	Mean,	106.920

SECOND SERIES.

Weight $Pd(NH_3Cl)_2$, gms.	Weight Pd, gm.	Atomic weight.
1.94722	0.98343	106.894
1.08649	0.54870	106.885
1.28423	0.64858	106.890
1.68275	0.85010	106.955
1.69113	0.85431	106.949
1.80805	0.91310	106.896
	Mean,	106.911
	Both series combined,	106.914

Calculated with H = 1, N = 14.01, Cl = 35.37.

Two determinations were also made by reducing the $Pd(NH_3Cl)_2$ to PdS, by heating in a stream of hydrogen sulphide. Results as follows:

0.71699 gm. $Pd(NH_3Cl)_2$ gave 0.47066 PdS; atomic weight, 107.07
1.31688 " " " 0.86445 " " " 107.07

These experiments are regarded as having only confirmatory value.

Since the results obtained are higher than those published by Keiser, who reduced palladammonium chloride by heating in hydrogen, the authors repeated his experiments in order to ascertain the causes of discrepancy. Fourteen determinations were made; showing, first, that the unpulverized chloride decrepitates, so that material is lost; and, secondly, that there is slight

volatilization of palladium. Keller and Smith also introduce evidence to show that Keiser's material was not pure.

—*Am. Chem. J.*, **14**, 4[illegible]

Nickel.—The elaborate investigation by Kruss and Schmidt upon the atomic weight of nickel, is based upon fractional distillation of carefully purified metal, as nickel-tetracarbonyl in a stream of carbon monoxide. The distillate, in ten successive fractions, furnished the nickel used in the actual determinations. First, an attempt was made at direct comparison with hydrogen by measuring the gas evolved during solution of the metal in acid. The results, however, gave values for Ni ranging from 57.7 downward to below 57, and this line of attack was abandoned. The common methods of converting Ni into NiO and of reducing NiO to Ni by reduction in hydrogen, were finally adopted. Thus, in fraction No. 1, 0.3722 gm. NiO gave [illegible] Ni, whence Ni = 58.81. In the same sample, 0.5870 Ni gave 0.7471 NiO, whence Ni = 58.66. The last weighed NiO reduced, gave the original 0.5870 gm. Ni again, and [illegible] as before for the atomic weight. Tabulated, the entire series of results is as follows, apparently with O = 16.

		Ni		
First fraction by reduction	58.81	[illegible]		
oxidation	58.66			
Second " reduction	58.23	[illegible]		
oxidation	58.30	[illegible]		
Third " reduction	58.3[illegible]	58.18	58.18	
oxidation	58.13	58.3[illegible]	58.18	
Fourth " reduction	58.38	58.[illegible]		
oxidation	58.5[illegible]	58.[illegible]		
Fifth " reduction	58.2[illegible]	58.12		
oxidation	58.5[illegible]	58.12		
Sixth " reduction	[illegible]	[illegible]		
oxidation	58.48	[illegible]		
Seventh " reduction	58.23	[illegible]	58.[illegible]	
oxidation	[illegible]	58.4[illegible]	58	
Eighth " reduction	58.61	58.[illegible]	[illegible]	58.[illegible]
oxidation	[illegible]	58.4[illegible]	58.[illegible]	[illegible]
Ninth " reduction	58.[illegible]	[illegible]		
oxidation	[illegible]	[illegible]		
Tenth " reduction	58.2[illegible]	58.[illegible]		
oxidation	58.2[illegible]	58.[illegible]		

The metal remaining in the tube after these ten fractions had been distilled off, was dissolved in weak hydrochloric acid, and the solution, filtered, was boiled with excess of potassium cyanide. The nickel was then precipitated in five fractions by bromine water, and the oxide thrown down, after thorough boiling and washing, was reduced to metal. The first and fifth of these fractions gave the following atomic weight data:

	Ni.
First fraction, by oxidation,	60.34
" " " reduction,	59.17
Fifth " " oxidation,	64.00
" " " reduction,	62.98

Hence the residual nickel, after the carbonic oxide distillations, has a distinctly higher atomic weight than that which had been distilled off. For a discussion of these results the original memoir must be consulted.

—*Ztschr. anorg. Chem.*, **2**, 235.

NICKEL ANALYSIS.*

By Stephen H. Emmens.

The substances usually submitted to analysis for the determination of the contained nickel may conveniently be classified as follows:

1. Regulus and minerals containing arsenic, viz., spiess and arseniferous ores of nickel. 2. Regulus and minerals containing no (or but little) arsenic, viz., matte, nickeliferous pyrrhotite and non-arseniferous ores of nickel. 3. Metallic nickel, nickel steel, German silver, and other alloys of nickel.

The principal published methods of analysis of these substances are summarized in tables I, II, and III.

It may be broadly stated that none of the analytical methods there set forth are satisfactory if practiced *in strict accordance with the published accounts*. The precipitation methods introduce a serious source of error by reason of the separated ferric hydroxid carrying down a portion of the associated nickel and cobalt.

* Eng. and Min. Jour., Nov. 26, 1892; with an addendum by the author.

The direct electrolysis of an acid solution containing copper iron, nickel, and cobalt cannot be relied upon to effect a complete separation of either the copper or the nickel and cobalt especially if a current of comparatively high voltage (e.g. from three Bunsen cells in series) be employed. And Miner's volumetric method must obviously fail in the presence of copper and iron.

In the absence, then, of any generally recognized and accepted system of accurate nickel analysis, Mr. Charles T. Miner (Princeton, 91), the chemist of the Emmens Metal Company

TABLE I.—SPEISS AND ARSENIFEROUS ORES

Operation	Reagent employed	Substance separated
A. Watts—*Dictionary*		
1 Fusion with reagent and lixiviation with water	$KNO_3 + Na_2CO_3$, or $Na + K_2CO_3$,	As
2 Dissolve and filter	$HCl + HNO_3$,	[illegible]
3 Nearly neutralize	Na_2CO_3 or NH_3, (CO_3),	
4 Precipitate and filter	CH_3CO_2Na or $CH_3CO_2NH_4$	[illegible]
Or 1 Dissolve	$HNO_3 + HCl$	
2 Filter and heat		[illegible]
3 Nearly neutralize	Na_2CO_3	
4 Precipitate and filter	$CH_3CO_2Na + Fe_2(CO_3)$	[illegible]
5 Acidulate	HCl	
6 Precipitate and filter	H_2S	[illegible]
7 Boil precipitate and filter	Na_2CO_3	[illegible]
B. Watts (*Dictionary* revised)		
1 Dissolve and evaporate	$HNO_3 + HCl$	
2 Dissolve and filter	HCl	[illegible]
3 Boil	$NaHSO_3$*	
4 Precipitate and filter	H_2S	[illegible]
5 Concentrate, precipitate and filter	$C_2O_4H_2$	[illegible]
Or 5 Evaporate, dissolve and filter	H_2O	
6 Gasify	[illegible]	
7 Precipitate and filter	$BaCO_3$	[illegible]
8 Precipitate and filter	H_2SO_4	[illegible]
9 Precipitate and filter	Na_2CO_3	[illegible]

* Instead of Na_2CO_3 is Na_2O.

TABLE II.—MATTE, PYRRHOTITE, AND NON-ARSENIFEROUS ORES.

Operation.	Reagent employed.	Substance separated.
A. Fresenius (Allen and Johnson)		
1. Dissolve and filter	$HNO_3 + H_2SO_4$	SiO_2 + insol
2. Precipitate and filter	H_2S	Cu
3. Peroxidize, precipitate, and filter	$HNO_3 + NH_3$	
4. Dissolve the precipitate	HCl	Fe
5. Precipitate and filter	$NH_3 + Na_2CO_3$ (or $(NH_4)_2CO_3 + CH_3CO_2H$)	
6. Repeat 4 and 5		
7. Alkalinize the combined filtrates from 3, 5, and 6	NH_3	
8. Acidify slightly, precipitate and filter	$HCl + H_2S$	Ni + Co
B. Cheney and Richards		
1. Dissolve and filter	$HNO_3 + HCl$	SiO_2 + insol.
2. Precipitate and filter	H_2S	Cu
3. Peroxidize and *begin* to precipitate	$HNO_3 + NH_3$	
4. Dissolve	CH_3CO_2H	
5. Boil, precipitate, and filter	Conc. sol. of HNa_2PO_4	Fe
6. Boil add reagent until odor of NH_3 is distinct, filter	KHO	(Ni + Co) phosphate
7. Dissolve the precipitate	H_2SO_4	
8. Alkalinize and electrolyze	NH_3	Ni + Co
C. Sutton—*Vol. Anal.*, 6th ed., p. 166.		
1. Dissolve and filter	HNO_3; or, $HNO_3 + HCl$	SiO_2 + insol.
2. Nearly neutralize	Na_2CO_3	
3. Dilute	H_2O (cold)	
4. Precipitate and filter	Freshly precipitated $BaCO_3 + NH_4Cl$	Cu + Fe
D. Moore.—Sutton's *Vol. Anal.*, p. 224.		
1. Dissolve and filter	$HNO_3 + HCl$	SiO_2 + insol.
2. Precipitate and dissolve	$Na_4P_2O_7$	
3. Acidify faintly	HCl	
4. Alkalinize distinctly	NH_3	
5. Convert the blue color into a yellowish tint	Standardized sol. of KCN	
6. Change to violet brown	Precipitate from $CuSO_4 + K_4Fe(CN)_6$ dis. in sol. of $(COONH_4)_2$	
7. Destroy color	Standardized sol. of KCN	Determination of Ni
E. Sperry—Peters' *Modern Copper Smelting.*		
1. Dissolve and evaporate	$HNO_3 + H_2SO_4$	
2. Dissolve and filter	$HNO_3 + H_2SO_4 + H_2O$	SiO_2 + insol.
3. Electrolyze		Cu
4. "		Ni

TABLE III.—METALLIC NICKEL, NICKEL STEEL, GERMAN SILVER, AND ALLOYS.

Operation.	Reagent employed.	Substance separated.
A. Thorpe—*Applied Chemistry.*		
1. Dissolve and evaporate	$HNO_3 + HCl$	
2. Dissolve and filter	HCl	C + insol.
3. Precipitate and filter	H_2S	Cu
4. Precipitate and filter	$CH_3CO_2Na + CH_3CO_2NH_4$	$Fe + Al$
5. Precipitate and filter	H_2S	$Ni + Co$
B. Clowes and Coleman.		
1. Dissolve and evaporate	HNO_3	
2. Dissolve and filter	H_2O	SnO_2
3. Precipitate and filter	H_2S	Cu
4. Add reagent till precipitate begins and dissolve	$Na_2CO_3 + HCl$	
5. Precipitate and filter	$CH_3CO_2NH_4 + H_2S$	Zn
6. Acidify and boil	HCl	
7. Precipitate and filter	$NaOH$	$Ni + Co$

has, in conjunction with myself, devised the following methods, which we find to be sufficiently trustworthy for all technical and commercial purposes.

METHOD A.—FOR SUBSTANCES HIGH IN NICKEL AND LOW IN COPPER AND IRON—*e. g.*, METALLIC NICKEL, BESSEMERIZED MATTE, NICKEL OXID, ETC.

Operation.	Reagent.	Separation.
1. Dissolve (about 2 gms.) and evaporate	$HNO_3 + HCl$, or fusion with $KHSO_4$	
2. Dissolve and filter	$HCl + H_2O$	SiO_2, C, etc.
3. Precipitate and filter	H_2S	CuS
4. Dissolve the washed precipitate and evaporate till white fumes are produced	$HNO_3 + H_2SO_4$	
5. Dissolve and electrolyze	$H_2O + HNO_3$	Cu
6. Boil filtrate from 3 and peroxidize	HNO_3	
7. Cool and make solution up to 400 cc.	H_2O	
8. Boil ½ of 7, precipitate and filter	NH_3	
9. Re-dissolve the precipitate	HCl	
10. Precipitate and filter	NH_3	
11. Dissolve and reduce the well-washed precipitate	$H_2SO_4 + Zn$	
12. Titrate	$KMnO_4$	Fe
13. Precipitate and filter $\frac{1}{10}$ (40 cc.) of 7	$NaOH$	
14. Dissolve the washed precipitate	Dilute H_2SO_4	
15. Make alkaline	NH_3	
16. Electrolyze		$Ni + Co$

METHOD B.—FOR SUBSTANCES HIGH IN IRON AND LOW IN NICKEL—*e. g.*, PYRRHOTITE AND ONCE-RUN MATTE.

Operation.	Reagent.	Separation.
1. 2. 3. 4. 5. 6. Same as in Method A.....		Cu
7. Precipitate and filter	NH_3	$Fe_2O_3.H_2O$
8. Boil the washed pp. and re-filter...	H_2O made faintly acid with H_2SO_4 or HCl	$Fe_2O_3.H_2O$
9. Precipitate and filter	$NH_4Cl + NH_3$	$Fe_2O_3.H_2O$
10. Add together the filtrates from 7 and 9, evaporate to small bulk, precipitate and filter..... ...	NaOH in large excess	
11. Dissolve the washed pp.	Dilute H_2SO_4	
12. Make alkaline.....	NH_3	
13. Electrolyze		Ni + Co

Method C.—Qualitative examination of pyrrhotite and other lean ores of nickel.

1. Reduce to fine powder.

2. Dissolve in *aqua regia;* evaporate to dryness; dissolve in HCl and H_2O; filter off from gangue and insoluble matter.

3. Pass H_2S through the solution to remove Cu.

4. Boil free of H_2S; peroxidize with HNO_3.

5. Precipitate the Fe with NH_3; boil; add HCl until the supernatant liquid is faintly acid; boil sharply for ten minutes.

6. Make strongly alkaline with NH_3 and note the color of the supernatant solution. If it be distinctly blue the percentage of nickel in the ore is commercially important.

7. If the solution be colorless, filter and boil down to a small bulk free from the odor of NH_3. Then add a few drops of a solution of potassium sulfo-carbonate, which will give a pink coloration if there be any trace of nickel in the ore.

N. B.—Test 7 is also useful for determining when the electrolytic separation of the Ni is complete in methods A and B. We find that the reaction is best observed when the solutions are neutral instead of being alkaline as recommended in text-books.

A distinguishing feature of our process is the treatment of the

precipitated ferric hydroxid with a minute quantity of acid. This has the effect of dissolving any Ni or Co hydrate that may have been carried down with the iron, and it is more efficient than the numerous tedious and troublesome repetitions of solution, precipitation, filtration, and washing necessitated by the older methods. At first sight, indeed, it may be doubted whether sulfuric or hydrochloric acid will unite with nickel in preference to iron, seeing that the latter metal oxidizes more energetically than the former; but the following thermochemical data (taken from Muir and Wilson's *Thermal Chemistry*) will make the matter clear:

Reaction	Heat generated (gram-calories)
Fe + O + SO_4 Aq	[illegible]
Ni + O + SO_4 Aq	[illegible]
Fe + Cl_2 + Aq	[illegible]
Ni + Cl_2 + Aq	[illegible]
Fe + O + H_2O	[illegible]
Ni + O + H_2O	[illegible]

It results from these figures that the heat of formation of the molecule of ferrous sulfate by the union of ferrous hydroxid with dilute sulfuric acid is 93,200—68,280 = 24,920 units, while that of nickel sulfate formed by the union of nickel hydrate with sulfuric acid is 80,050 - 60,840 = 20,110 units. Under these conditions, therefore, Berthelot's law of maximum work applies to the formation of nickel sulfate in preference to ferrous sulfate. If HCl be the acid the figures are:

Formation of nickel chlorid	[illegible]	[illegible]
ferrous	[illegible]	[illegible]

In the particular case under consideration the replacement of nickel is still more marked, as, owing to the iron being oxidized, its basic efficiency is lessened. The heat of formation of formula weight of acid, as given by Berthelot (*Thermochemie*, I, 384), are:

Formation of ferric chlorid	[illegible]
sulfate	[illegible]

In concluding these brief notes I may remark that the text-books contain very few examples of the analyses of commercial

TABLE IV.—METALLIC NICKEL, NICKEL MATTE, NICKEL OXID, ETC.

Substance.	Manufacturer.	Date.	Analyst or authority.	Percentage composition.							
				Ni.	Co.	Total Ni and Co.	Fe.	Cu.	S.	C, SiO_2, and other impurities.	
Matte (Swedish)	.....	.....	Wagner's *Chem. Tech.*, 8th ed.	.....	.....	26.00	16.33	31.67	26.00		(1)
" (Sudbury)	Canadian Copper Co.	1889	F. L. Sperry	14.84	0.27	14.71	31.00	27.06	26.90	0.92	
" "	" " "	"	" "	13.04	0.20	14.04	31.47	26.76	27.00	0.95	
Bessemerized Matte, (Sudbury)	" " "	1892	Canadian Copper Co	.....	.....	35.93	1.09	40.98	19.71	2.29	(2)
" (New Caledonia)	.....	.....	Thorpe's *Dict. of Appl. Chem.*	.....	.....	67.17	11.90	.....	17.08	3.85	
"Fonte," (New Caledonia)	.....	.....	" " " "	.....	.....	67.95	25.87	.....	1.95	2.90	
Nickel oxid (Sudbury)	Orford Copper Co.	1891	Hunt and Clapp	.....	.....	74.60	1.51	1.25	.....	1.45	
Nickel oxid (New Caledonia)	Société le Nickel	"	Ledoux	.....	.....	77.92	0.25	0.09	.....	.....	
Artificial nickel ore	.....	"	E. F. Wood	.....	.....	48.23	23.87	Trace	0.264	27.636*	
Nickel (German)	.....	.....	Lassaigne (Watts' *Dict.*)	56.75	.....	56.75	12.55	27.50	.....	3.70	
" "	.....	.....	" " "	54.60	.....	54.60	11.30	30.10	.....	4.00	
" (English)	.....	.....	" " "	73.30	22.10	95.40	1.00	Trace	.....	3.00	
" (New Caledonia)	Christofle	1881	Christofle and Bouilhet	.....	.....	97.75	(Mn) 0.36	.....	.....	1.79	
Disc Nickel (New Caledonia)	.....	.....	Thorpe (*Dict. of Appl. Chem.*)	.....	.....	98.83	0.72	.....	.....	0.45	
Cast "	.....	.....	Gard (Wagner, 13th ed.)	97.44	Trace	97.44	0.301	.....	0.104	2.155	
Sheet " (German)	Fleitman	1891	F. P. Dewey	97.050	1.858	98.908	0.829	0.498	0.012	0.042	(3)
Rolled anode nickel	"	"	" "	97.63	1.19	98.82	0.75	0.15	0.04	0.24	(4)
Disc "	Société le Nickel	"	" "	97.38	1.70	99.08	0.06	0.68	0.013	0.167	(5)
Cube "	H. Wigins & Co.	"	" "	96.757	1.586	98.343	0.32	0.113	Trace	1.224	
Grain "	J. Wharton	"	" "	94.988	0.856	95.844	0.354	0.047	Trace	3.755	(6)
" "	Orford Copper Co.	1892	" "	96.29	0.93	97.22	1.92	0.20	0.104	0.556	(7)
Cast nickel anode	Hanson & Van Winkle Co	"	" "	83.68	Trace	83.68	7.10	0.15	0.19	8.88	(8)
" " "	Zucker & Levant	1891	" "	82.776	1.133	83.909	12.091	0.103	0.05	3.847	(9)

(1) Average of three assays.
(2) " " " "
(3) "It showed by qualitative analysis slight traces of arsenic, antimony, and aluminum, and a perceptible amount of silicon. No other metal or phosphorus was found." Note by Mr. Dewey.
(4) "Showed some silicious residue." Note by Mr. Dewey.
(5) "A small amount of hard, gritty grains left on dissolving the metal." Note by Mr. Dewey.
(6) "It showed by qualitative examination the slightest traces of arsenic and antimony, some aluminum, and considerable silicon and calcium. Distinct grains of slag were found. No other metal or phosphorus was found." Note by Mr. Dewey.
(7) There is some Si and considerable As in this sample." Note by Mr. Dewey.
(8) "It contained a considerable amount of tin, probably seven per cent. There is also considerable silicon present." Note by Mr. Dewey.
(9) "It showed on qualitative analysis slight traces of arsenic and antimony, some aluminum and calcium, and considerable silicon. No other metal or phosphorus was found." Note by Mr. Dewey.
* Including oxygen.

nickel, matte, etc. I therefore add the table 4 above, which will serve to indicate the general character of the substances that the nickel analyst is called upon to examine nowadays.

ADDENDUM

In operation 8 of method B Mr. Mixer finds that the best results are obtained by adding dilute acid, drop by drop, to the boiling precipitate until the iron begins to be attacked. If this be done so that only a small quantity of the iron enters into solution operation 9 becomes unnecessary and the whole solution may be added to the filtrate from 7, the ultimate presence of a little floating ferric hydrate being unimportant. We have also discovered that a solution of ferric sulfate may be used instead of dilute acid for extracting the nickel from the precipitated iron. The feasibility of this is shown by the following thermal values:

	Calories
$Fe_2O_3 + 3H_2SO_4$, Aq.	[illegible]
$3Ni(OH)_2 + 3H_2SO_4$, Aq.	[illegible]

ON THE PROPERTIES OF HYDROGEN PEROXID SOLUTIONS.*

By Henry P. Talbot and Herbert R. Moody, S. B.

The information to be found in the present literature of hydrogen peroxid regarding either the preparation of concentrated solutions of that reagent, or the properties of such solutions after their preparation, is meager and unsatisfactory.

Thenard,† the first to identify this chemically interesting substance, concentrated the dilute solutions which he obtained by evaporation *in vacuo* over sulfuric acid. He succeeded in attaining a high degree of concentration, but this method is not suitable for the treatment of large quantities of solution. Since Thenard's work, the most important contribution to this branch of the subject is that made by Hanriot.‡ He found that on partially freezing a solution of hydrogen peroxid the liquid remaining after the removal of the ice contained a larger proportion of peroxid than the original solution, and took advantage of this fact as a means of concentration. In this way he obtained solutions which would yield of themselves seventy to eighty times their own volume of oxygen upon complete decomposition.

Hanriot subsequently found§ that dilute solutions of hydrogen peroxid could be concentrated by distillation at greatly reduced pressures without serious loss by decomposition, and in this way

* From the Technology Quarterly.
† Ann. chim. phys. [illegible]
‡ Compt. rend. [illegible]
§ Compt. rend. [illegible]

under a pressure of three mm., he obtained a solution which would evolve 267 times its own volume of oxygen, and states that no appreciable decomposition takes place below 150 volumes.

The writers of the present article have had occasion to deal with commercial solutions and to prepare from them concentrated solutions in considerable quantities. The facts here presented are those which have been observed during the progress of this work, which have a bearing upon the questions in hand.

The commercial solutions found on the market varied in strength from eighteen volumes to twenty-three volumes, if only those are included which were known to have been freshly prepared. Others were found which were as low as eight volumes.

Kingzett* has called attention to the variations in custom as regards the expression of the value of solutions of hydrogen peroxid. He states that a fifteen-volume solution is properly "one which of itself, by complete decomposition, will furnish fifteen times its own volume of oxygen at ordinary temperature and pressure"; but he points out that the American custom designates as a fifteen-volume solution one which will evolve fifteen times its own volume of that gas when brought into contact with a substance which itself furnishes one half the volume of oxygen. It is evident that the latter solution has but one-half the strength of the former. Since the latter method of expression is that used commercially, it will be employed throughout this article; but attention is called to the fact that for purposes of oxidation the amount of available oxygen is but one-half that indicated by the commercial name.

A suggestion made by Dr. F. H. Williams, that the strength of solutions should be uniformly expressed in percentage of hydrogen peroxid, is one which, if generally adopted, would avoid the confusion now existing, and would be more readily understood by physicians.†

In view of the fact that hydrogen peroxid is generally recommended as a useful reagent in analytical chemistry, it is desirable that something should be known regarding the purity of the solu-

* Journal of the Society of Chemical Industry, 9 (1890), 4.

† It may be noted here, for purposes of comparison, that a 20-volume solution (as the term is used in this article), contains 2.9 per cent. of hydrogen peroxid; a 50-volume solution, 6.9 per cent., and a 100-volume solution, 13.4 per cent., by weight.

tions which are readily available. Of the eight commercial samples examined, none were suitable for analytical purposes without purification, and most were so impure that their use would be ill advised even though blank analyses had been made. They contained hydrochloric, sulfuric, phosphoric, and hydrofluosilicic acids, sugar and glycerin. The two latter substances were present in largest amounts in the sample prepared for medicinal use. Barium, calcium, aluminum, and magnesium were also found.

The amount of phosphoric acid, as found by precipitation with ammonium molybdate and reprecipitation as magnesium ammonium phosphate, was in one sample 0.16 per cent., in another 0.13 per cent. of the solution by weight: an amount capable of doing much mischief in analytical work.

Fifty cubic centimeters of a commercial sample evaporated on a water bath left a residue weighing 0.0588 gm., of which [illegible] gm. remained after ignition. This sample contained sulfuric, phosphoric and hydrofluosilicic acids and barium. A sample intended for medicinal use yielded a syrupy residue on evaporation, the amount from fifty cc. weighing 0.4400 gm. at [illegible] it was still syrupy, but had the odor of caramel and the weight had fallen to 0.4195 gm.; upon ignition over a Bunsen burner glycerin distilled, and the sugar was charred and burned; the residue, after treatment with ammonium nitrate, being white and weighing 0.0164 gm. This residue was largely barium chloride.

The presence of hydrofluosilicic acid in these solutions is also a menace to analytical work since, upon subsequent neutralization of the acid, the precipitation of an insoluble hydrofluosilicate or of silicic acid takes place, either of which is likely to interfere with gravimetric processes. The amount of hydrofluosilicic acid found in one sample, a twenty two volume solution, was [illegible] per cent. of the solution by weight. The acid was precipitated and weighed as potassium silicofluoride and was also determined from the amount of silica present.

An order placed with one of the manufacturers for a preparation of hydrogen peroxid which should be sufficiently pure for analytical purposes resulted in the production of a solution which was free from phosphoric acid and yielded but [illegible] gm. of ignited residue from fifty cc. of the sample. The amount of silica

found was 0.0026 per cent,, and only minute quantities of calcium and aluminum, with a little organic matter, were present. This sample might have been used for analytical purposes without further purification.

As a method of purification of the commercial solutions, the following was found most successful: The solution was treated with about ten per cent. by volume of alcohol, after which barium hydrate in powder was added to distinctly alkaline reaction. The precipitate, containing most of the impurities, was then filtered off with the help of a gentle suction, using a porcelain filter plate, and the excess of barium removed by the addition of sulfuric acid in excess. The barium sulfate was allowed to settle, and the supernatant liquid quickly filtered as before. The loss of peroxid is small if the first filtration is hastened, thereby reducing the time during which the solution remains alkaline. By this method the amount of silica was reduced from 0.028 per cent. to 0.003 per cent. of the solution by weight. The alcohol may be removed by distillation at reduced pressure, and the residual solution may then be used for analytical purposes without further precaution than the customary blank analysis. The barium hydrate used should be as free from carbonate as possible.

It was subsequently found that a solution thus treated could be further purified by distillation, but only at a great sacrifice of material. This will be referred to again.

The addition of ferric chlorid and subsequent precipitation with barium hydrate cannot be employed as a means of purification, since the formation of ferric hydrate in the solution causes prompt and complete decomposition of the peroxid which the previous addition of alcohol, ether, or their mixture does not hinder.

It was found that the concentrated solutions containing phosphoric and hydrofluosilicic acids, when shaken with ether, gave up a portion of these acids together with the peroxid. Purification by this means, therefore, was not possible. Experiments proved that for practical purposes concentration by distillation at reduced pressure is preferable to freezing. The distillations were made in glass—an ordinary round-bottomed flask or a boiling flask, a Liebig condenser and glass receiver comprising the apparatus. The stoppers were of rubber. For distillations at pres-

sures less than that of the atmosphere the apparatus was connected with a suction pump capable of reducing the pressure to thirty or forty mm. To prevent violent bumping, it was usually necessary to insert a capillary tube and draw a slow current of air through the solution in the boiling flask. This bumping is, in itself, an evidence that the decomposition of the peroxid is slight. To prevent decomposition by over-heating, the flask was placed in a water bath.

The rate at which the solutions concentrate under varying conditions may be learned from the tables below. The column marked "Per cent. total loss" expresses the percentage of hydrogen peroxid which the solution has lost during the distillation and is calculated upon the theoretical concentration, which in turn, is estimated from the decrease in volume of the solution in the boiling flask, and takes no account of the small quantity of peroxid which passes into the distillate. The commercial solution employed was a twenty-volume solution, containing as impurities, phosphoric, hydrofluosilicic, sulfuric, and hydrochloric acids, and a small quantity of iron.

The rate of concentration of the residual solution in the boiling flask was determined by titration with potassium permanganate. One cubic centimeter was removed with a pipette, diluted with fifty to seventy five cubic centimeters of distilled water, acidified with sulfuric acid, and titrated to the customary end point. This was the method employed in all determinations mentioned and a comparison of this method with a gas volumetric process will be made at the close of the article.

CONCENTRATION BY DISTILLATION

I				II			
At atmospheric [illegible]				[illegible]			
Vol. of Distillate [illegible]	Strength of Distillate [illegible]	Strength of Residual Solution [illegible]	Per cent Total loss	Vol. of Distillate [illegible]	Strength of Distillate [illegible]	Strength of Residual Solution [illegible]	Per cent Total loss
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]	[illegible]	[illegible]	[illegible]
				[illegible]		[illegible]	[illegible]

Original volume = [illegible]

Original strength [illegible]

CONCENTRATION BY DISTILLATION.

III. UNDER PRESSURE OF 140 MM.				IV. UNDER PRESSURE OF 30 MM.			
Vol. of Distillate, cc.	Strength of Distillate, vols.	Strength of Residual Solution, vols.	Per cent. Total loss.	Vol. of Distillate, cc.	Strength of Distillate, vols.	Strength of Residual Solution, vols.	Per cent. Total loss.
55	0.5	23.1	0.0	50	0.9	22.0	2.7
55	0.8	26.8	0.8	50	0.9	25.2	5.0
55	0.8	30.8	9.4	50	0.9	29.6	6.9
55	0.8	39.0	12.1	50	0.9	37.8	5.5
65	1.2	63.6	8.4	50	0.9	49.8	7.7
60	2.0	138.7	4.6	50	1.3	77.2	2.7
20	6.3	189.4	7.0	50	9.4	151.2	4.8

Original volume = 400 cc.
Original strength = 20 vols.

Original volume = 400 cc.
Original strength = 19.84 vols.

CONCENTRATION BY DISTILLATION.

V. AT ATMOSPHERIC PRESSURE WITH THE ADDITION OF PHOSPHORIC ACID.				VI. AT 390 MM. PRESSURE WITH THE ADDITION OF PHOSPHORIC ACID.			
Vol. of Distillate, cc.	Strength of Distillate, vols.	Strength of Residual Solution, vols.	Per cent. Total loss.	Vol, of Distillate, cc.	Strength of Distillate, vols.	Strength of Residual Solution, vols.	Per cent. Total loss.
60	0.6	21.1	10.8	40	0.6	21.5	4.0
60	0.7	24.5	15.0	50	0.6	22.3	13.9
60	0.8	27.9	23.5	50	0.9	26.5	14.2
60	0.8	35.6	29.2	50	1.3	31.5	18.0
65	1.9	54.2	35.9	50	0.9	37.8	24.7
60	3.1	69.0	70.0	60	1.9	53.9	32.9
25	8.5	0.3	99.9	50	4.1	107.3	33.2
.....	.....	.....	.....	45	19.2	6.3	99.8

Original volume = 400 cc.
Original strength = 20.2 vols.

It is obvious that the figures representing the loss by decomposition in these tables must be approximate only, since this is influenced by the amount of mechanical agitation of the solution and the length of time which it has stood at the temperature of the laboratory previous to distillation. Another factor which influenced the results when the distillation was made at very low pressure, was the removal of uncondensed steam through the suction pump, the low temperature at which the solution boils (36° C. for thirty mm. pressure), making it difficult to effect complete condensation. Tables I to IV, inclusive, show approximately the rate of concentration under varying conditions, and demonstrate the fact that strong solutions may be prepared by

distillation at a pressure of thirty to forty mm. without serious loss. The addition of certain non-volatile substances as preservatives during distillation was not attended with a large degree of success. Sulfuric acid, boracic acid, phosphoric acid and glycerin were each tried; but, of these, phosphoric acid alone appeared to hinder decomposition, and that only within certain limits, as shown by Tables V and VI. At the lower pressure the results are more favorable than in the absence of the acid until the solution is highly concentrated. Ten cubic centimeters of a saturated solution of phosphoric acid were used in the first case (Table V), and five cubic centimeters in the second. As the action of the remaining acids and glycerin it may be said that they appear to hinder decomposition only at the first after which they increase rather than lessen the loss. It may be mentioned that the presence of an excess of caustic alkali or ammonia causes prompt and complete decomposition of the peroxid.

The figures given in Tables III and IV show that appreciable quantities of hydrogen peroxid pass into the distillates as the solution in the boiling flask concentrates. This fact may be utilized as a method of purification of the peroxid solutions from most of the foreign ingredients. It is not wholly successful since the hydrofluosilicic acid is present in such large quantities that at the point at which the peroxid begins to pass over in any considerable quantity, this acid is decomposed and silicon fluoride passes into the distillate with the reformation of hydrofluosilicic acid. This was made evident by the accumulation of silica as in the condenser from the partial decomposition of the silicon fluorid by condensed steam. The distillate is free from other impurities than the hydrofluosilicic acid, and by a second concentration a very pure solution could doubtless be obtained, but at a great sacrifice of material. By subjecting the filtrate from the precipitation with barium hydrate in the presence of alcohol, as already described, to distillation at reduced pressure, it is easy to obtain a distillate which, while weak, contains a minute quantity of hydrofluosilicic acid. It may be concentrated after the addition of such a quantity of sulfuric acid that when concentrated to a twenty volume solution it shall contain about [illegible] per cent by weight of the acid.

The statement is made by Hanriot* that pure hydrogen peroxid gives an acid reaction; but distillates prepared as just described, capable of evolving nine volumes of oxygen, are but very feebly acid (which may be accounted for by the presence of hydrofluosilicic acid and hydrofluoric acid in very small quantities), and when made neutral by a drop of an alkali solution remain so, even though the amount of peroxid is undiminished. It appears to us that the statement of Hanriot cannot be correct, although he claims to have proved the absence of acid in the solutions tested.

The data already presented make it evident that the preparation of concentrated solutions of hydrogen peroxid from the commercial solutions is a matter of but little difficulty, unless the complete absence of foreign matter is required. The writers have prepared considerable quantities of solutions, varying in strength from thirty to five hundred and eighty-eight volumes. It has generally been found expedient to concentrate the solution to about fifty volumes before making any attempt to purify, unless the purification is accomplished by precipitation with barium hydrate, in which case the precipitation must precede the concentration. A convenient procedure by which the impurities may be largely removed is the following: The solution is made neutral with caustic potash (as free from carbonate as possible), and the precipitate of silica, potassium silicofluorid and other impurities is allowed to settle. This takes place promptly. The supernatant liquid is then decanted through a ribbed filter, and the last portion, which contains the precipitate, and therefore filters slowly, is rejected, or preserved for re-concentration if necessary. In this way a solution is obtained which is free from most of the original impurities, but contains potassium salts of the acids present. The filtered liquid should be made acid with sulfuric acid as soon as filtered, to prevent the decomposition of the peroxid in neutral solution, and the amount of acid added to a fifty-volume solution should be about 0.5 per cent. by weight. An equivalent amount of hydrochloric acid may be substituted for the sulfuric acid.

In the preparation of solutions above fifty or sixty volumes it

*Compt. rend., 100 (1885), 172.

	[illegible]	[illegible]	[illegible]				
	[illegible]	[illegible] per cent	[illegible]				
[illegible]	[illegible]	[illegible] per cent	[illegible]				
	Commercial solution concentrated and purified by Kroll	[illegible]	[illegible]				
[illegible]	Commercial solution concentrated and purified by Kroll	Nearly neutral	[illegible]				
[illegible]	Commercial solution concentrated at reduced pressure	[illegible] per cent	[illegible]				
[illegible]	Commercial solution concentrated at reduced pressure	[illegible] per cent	[illegible]				
[illegible]	Commercial solution concentrated	Alkaline with Kroll	[illegible]				
[illegible]	Commercial solution concentrated	Alkaline with NH_4OH	[illegible]				
[illegible]	Commercial solution concentrated at reduced pressure	[illegible] per cent	[illegible]				
[illegible]	Commercial solution concentrated at reduced pressure	[illegible] per cent	[illegible]				
11	Prepared from No. [illegible] by dilution	[illegible] per cent	[illegible]				
12	Prepared from No. [illegible] by dilution	[illegible] per cent	[illegible]				

is expedient to purify with caustic potash, if this is the method used, before concentrating beyond this point, since the stronger solutions decompose with great rapidity as soon as the acid is neutralized.

The loss of strength is very gradual even in highly concentrated solutions, provided there is free acid present. The accompanying table will furnish data in support of this statement.

A comparison of the solutions numbered 2 to 8 inclusive, shows that those which have been prepared by the evaporation of commercial solutions, without neutralization, maintain their strength for a considerable length of time; while those which have been made neutral decompose in a few days, and an excess of alkali causes immediate deterioration. In some cases the decomposition upon the addition of the alkali was spontaneous and accompanied by a marked evolution of heat. Solutions which have been even partially neutralized by alkali carbonates deteriorate during the neutralization, the carbonic acid evolved acting mechanically to destroy the peroxid.

It is also evident from the foregoing table that solutions of less strength than 100 volumes may be kept for some time at the temperature of the laboratory; but an examination of solutions 9 to 12, inclusive, shows that the highly concentrated solutions are preserved for much longer periods if kept at low temperatures. The stronger solutions—from 50 to 400 volumes—find their chief use in medicine and dentistry, and a loss of ten per cent. in strength does not interfere with their practical efficiency. A glance at the table shows that, even in case of the strongest solution, several days elapse before the value of the solution diminishes to that extent. It should be mentioned that these solutions were stoppered, and were only disturbed when the samples were removed for analysis. The deterioration would have been slightly greater if the solutions had been frequently exposed to the air or frequently shaken; but the fact is demonstrated that, if reasonable precautions are taken, even 400-volume solutions, if freshly prepared, may be preserved sufficiently long to admit of their practical use by physicians in extreme cases. They should be carefully stoppered, kept at a low temperature, out of contact with daylight, and should be disturbed as little as possible. To what

extent the permanency of the strong solution may be increased by the addition of the preservatives recommended by Kingzett for commercial solutions, the writers have not yet determined.

Finally, a few words regarding the practical value of the permanganate method for the determination of the amount of the hydrogen peroxid present. If, as has been stated, the oxygen evolved during the treatment with permanganate is not furnished equally by that reagent and the hydrogen peroxid, the titration should not yield accurate results. For the purpose of comparison, the amount of oxygen evolved by the solution alone was determined with the aid of the following apparatus: A boiling flask, of thirty cc. capacity was connected at its neck, by means of a T tube, with a carbonic acid generator, and with a two cc. pipette. The delivery tube from the boiling flask was connected with a Mitscherlich bulb surrounded by ice, and that, in turn, with an azotometer filled with a caustic potash solution (sp. gr. 1.27). The air was first expelled from the apparatus by a current of carbonic acid, after which the stopper of the flask was removed to insert the hydrogen peroxid (two cc.), and the small quantity of air introduced was again removed. The introduction of the peroxid was delayed until the greater portion of the air had been expelled, to prevent possible decomposition due to the contact with the carbonic acid for a longer time. Finally, two cc. of a solution of caustic potash (sp. gr. 1.27) was admitted through the pipette and T tube, which caused immediate evolution of oxygen. A gentle pressure of carbonic acid was maintained, and the flask heated in an oil bath until the solution had completely evaporated. The Mitscherlich bulb acted as a condenser, but no trace of undecomposed peroxid could be found in the condensed liquid. The oxygen passed into the azotometer and was measured, transferred to a Hempel pipette, the oxygen absorbed in potassium pyrogallate, and the small amount of air deducted. The residual volume was corrected for temperature and pressure. The results were as follows:

A solution which, from the titration with potassium permanganate, should evolve 10.08 volumes of oxygen at 0° and 760 mm., was found, by the gas-volumetric method just described, to evolve 10.12 and 10.22 volumes (corrected), the variation being 0.4 and

1.4 per cent. respectively; showing that for practical purposes the results obtained by titration with a solution of potassium permanganate, which has been standardized against iron wire, are sufficiently accurate. No further comparisons have yet been made of this gas-volumetric method with other methods; but the apparatus is so easily constructed, and the process is so simple and rapid, that it commends itself as a ready means for the determination of the amount of oxygen which the peroxid solution alone will furnish.

In conclusion, the writers desire to express their indebtedness to Dr. T. M. Drown for valuable suggestions and kind interest throughout the work.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.
JULY, 1892.

NEW BOOKS.

Manual of Qualitative Blowpipe Analysis by Endlich.*—This is one of the late works on blowpipe analysis, and justly takes rank with Brush, Platner, and Wöehler. Special mention is made of the physical properties of the substance, and minute directions are given for those who depend upon self-instruction. Among the more recent tests are the reducing action of stannous chlorid, the treatment with potassium bisulfate, and the iodids with sulfur. It will prove a valuable aid to those teaching the subject.

D.O'B.

A System of Instruction in Qualitative Chemical Analysis.†—The arrangement of this work is quite different from the conventional text books on qualitative analysis. The introduction, though, gives us the warrant for the course of the author, who embodies here the results of a score of years spent in teaching chemistry. The instructor at the College of Pharmacy occupies an elevated rostrum, in full view of every student in the room. Each one is given a portion of the same solution and works with the instructor, using a parallel set of apparatus.

* Published by the Scientific Publishing Co., New York. 456 pp.; price, $4.00.

† A System of Instruction in Qualitative Chemical Analysis. By Arthur H. Elliott Ph.D. Published by the Author. College of Pharmacy of City of New York.

Full explanations are made of each step in the separations. Following out the plan pursued in the author's laboratory, we find first, directions for separations, then come reasons for steps involved, followed by tabulated schemes, and finally, the individual tests for each metal in a group are given at the close of that group. A unique feature of the book is the grouping of "commercial compounds" at the end of each metal, as, for example, "cream of tartar," "pearl-ash," "Rochelle salt," etc., under potassium. Especially good are the explanations of the facts upon which the separations are based. Though written primarily for students who expect to follow pharmacy, and we find here and there references to the "U. S. P.," an authority not recognized by the ordinary analytical chemist, the book is well adapted for use with any class of students in qualitative analysis.

A. H. W.

NOTES.

If we are to judge from the manuscripts received, and from comments made upon it, the new system of spelling chemical words has come to stay. The Bureau of Education at Washington has published the report in chart form for the use of Preparatory and High Schools. In an editorial Dr. Edward C. Kirk of the *Dental Cosmos* says: "The *Dental Cosmos* will adopt the new method as its standard for the spelling of chemical terms commencing with the issue for January, 1893, and we respectfully urge upon our contributors the propriety of gaining a familiarity with the revised nomenclature by a study of the report. . . . In this connection we desire to call attention to the dropping of the final *e* in the word *dentine*, the spelling *dentin* being the term used in both the Century Dictionary and Foster's Medical Dictionary, and it has been adopted as the preferred form by the editors of Funk and Wagnalls Standard Dictionary."

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TECHNICAL ESTIMATION OF MANGANESE IN ORES.

BY ALBERT H. LOW.

PREPARE the following solutions: A standardized solution of potassium permanganate, approximately one-tenth normal. A solution of oxalic acid containing about 11.46 grams of $C_2O_4H_2,2H_2O$ per liter. Determine the exact strength of this solution by titrating with the permanganate in the presence of hot, dilute sulfuric acid in the usual manner, and then calculate its value in manganese on the basis that $C_2O_4H_2,2H_2O = Mn$. It will be found that one cc. will equal about 0.005 gm. of Mn, or about one per cent. when 0.5 gm. of ore is taken for analysis. A saturated solution of bromin in cold water. Always keep an excess of bromin in the bottle. Under the conditions to be described, twenty-five cc. of this solution will precipitate about thirty-five per cent. of manganese.

Method of Analysis.

Treat 0.5 gm. of the ore in a sixteen ounce flask with whatever acids are necessary to decompose it. Usually five to ten cc. of hydrochloric acid or aqua regia are sufficient. Boil until the free acid is nearly gone. This may be accomplished in two or three minutes by manipulating the flask over a naked flame. Dilute with about seventy-five cc. of hot water and add an excess of ZnO. Boil to effect complete neutralization of the acid. Now add an excess of the bromin solution, (usually twenty-five cc., never more than fifty cc.), and boil for a minute or two until the excess

is expelled, as indicated by the disappearance of the red fumes. An excess of ZnO should still be observed in the bottom of the flask. Filter, using a filter about five inches in diameter and wash flask and precipitate several times with hot water. Place the washed precipitate, together with the filter, back in the flask and add a sufficient amount, say fifty cc., of dilute sulfuric acid (1 to 9). Run into this mixture, from a burette, what is judged to be an excess of the oxalic acid solution, remembering that one cc. equals about one per cent. of Mn. Heat the mixture to boiling and then, if necessary, add more oxalic acid so as to effect complete solution of the precipitate. Now dilute somewhat with hot water and titrate the excess of oxalic acid with the permanganate solution. The number of cc. of oxalic acid actually consumed by the MnO_2 is thus arrived at, from which the percentage of manganese is then calculated. The entire analysis need not occupy more than twenty minutes. None of the ordinary constituents of ores interfere with the method and the results obtained are very satisfactory.

Of course, other reducing agents can be used in place of the oxalic acid solution. When the latter is not at hand a weighed amount of the double sulfate of iron and ammonium will be found convenient.

TECHNICAL ESTIMATION OF LEAD

By Albert H. Low

Provide three wash bottles containing the following mixtures respectively:

Distilled water, or, at least, chlorin free water.

Dilute sulfuric acid. One part C. P. acid to nine parts chlorin free water.

Chlorid of ammonium. Make a saturated solution of the commercial chlorid in common water, transfer this to the wash bottle as required, and heat to boiling for use.

Treat one gm. of the ore in a covered Griffin beaker of about 150 cc. capacity with ten cc. of a mixture of equal parts strong pure nitric acid and water. Heat carefully until the ore is perfectly well decomposed and then add ten cc. of pure strong sulfuric acid

and heat strongly until all the nitric acid is expelled and the sulfuric acid is boiling freely. This is best done over a small naked flame, taking care that the flame does not touch the beaker above the liquid. A 250 cc. flask has some advantages over a beaker for this decomposition, but is harder to wash out subsequently. Cool and add ten cc. of the above dilute sulfuric acid. Then add two gms. of Rochelle salt roughly weighed, or even guessed at. When this is dissolved add forty cc. of distilled water and heat to boiling. Allow to stand and settle two minutes and then filter and wash with the dilute sulfuric acid. Now spread the filter out carefully on a watch-glass and wash the contents back into the beaker with a stream of the boiling hot chlorid of ammonium solution. Heat the beaker again until all the sulfate of lead has dissolved, adding more chlorid of ammonium if necessary. Again filter, receiving the filtrate in a clean flask, and wash the filter thoroughly with the hot chlorid solution. Small amounts of sulfate of lead may be easily dissolved upon the original filter, without removing from the funnel, by simply washing with the hot chlorid solution. Place in the filtrate three pieces of sheet aluminum, each about one-sixteenth of an inch thick by five-eighths of an inch wide and an inch and three-quarters long. The aluminum should be the purest obtainable, as the commercial article leaves an appreciable residue of silicon on dissolving. Heat the contents of the flask to boiling. If the bulk of the filtrate has been kept down to 75 or 100 cc., the lead will be completely precipitated with five minutes' boiling. Remove from the heat and shake the mixture around to collect the lead. The aluminum should appear clean, with but little lead adhering to it. Fill the flask with cold water and transfer the entire contents to a large casserole. Wash the lead twice by decantation, and, after filling up the casserole the third time, remove the aluminum with the hand, rubbing off any adhering lead under water. Again decant and then rinse the lead into a small porcelain dish. Pour off the water and, with an agate pestle, collect the lead as nearly as practicable into one piece and press it into a thin, hard sheet. Wash this once or twice with distilled water and then with alcohol. Dry the lead carefully, which should not cause any oxidation whatever, and then

brush it into the scale-pan and weigh. The lead is practically free from silver, gold, copper, antimony, bismuth, arsenic, etc. A deduction of three per cent. is a fair allowance for arriving at the fire assay of a pure ore of the same grade. As but little of the aluminum is dissolved, the same pieces may be used repeatedly.

DETERMINATION OF THE ALKALIES IN SILICATES.

By Albert H. Low.

The following scheme is given more as a suggestion than as a description of a well-established method. The author had occasion to make some alkali determinations in a hurry, without great regard to extreme accuracy. J. Lawrence Smith's method was out of the question as all the carbonate of calcium at hand was too impure to be available. A consideration of the fact that in the author's method for zinc, (described in the Sept. 1895 number of this JOURNAL), all the zinc is extracted from a dried residue containing the substances from which it is ordinarily difficult to effect a good separation, led to the idea that a similar scheme might be as successfully applied to the case of the alkalies. The following method was then devised and tried with satisfactory results. If the bulks of the various filtrates, etc., are kept as small as possible, and the evaporations conducted with care over direct heat, the time required is considerably less than in Smith's method.

Treat one gm. of the finely powdered silicate by warming gently with pure strong hydrofluoric acid and a little sulfuric acid in a 100 cc. platinum dish until decomposition is complete. Evaporate to dryness and heat until the fumes of sulfuric acid have nearly ceased coming off. Cool, and add a little ammonia water and boil. See that a good disintegration is effected. Filter washing with a little hot water. Acidify the filtrate strongly with hydrochloric acid and add as small an excess as practicable of a solution of barium solution. Heat to boiling and filter washing with hot water. Evaporate the filtrate to dryness in platinum and ignite gently to expel ammonium salts. Cool, add a little carbonate of ammonium and ammonia water, boil and filter washing with hot water. Evaporate the filtrate to dryness in a weighed platinum

dish. This gives the combined chlorids which are separated in the usual manner.

As the author had but little time to investigate as to the accuracy of this method he sent a description to Dr. W. F. Hillebrand, of the U. S. Geological Survey at Washington, with the request that it be compared with the method in use. Dr. Hillebrand kindly complied and sent the following figures as the results of his analyses of two different samples of rock:

	NO. I. Per cent.		NO. II. Per cent.	
	K_2O.	Na_2O.	K_2O.	Na_2O.
Smith's method,	1.95	4.09	0.32	3.53
Low's "	1.91	4.10	0.35	3.55

Dr. Hillebrand suggests that his results by Low's method may be a trifle high, owing to the presence of a trace of potassium permanganate in his hydrofluoric acid, and, on the other hand, a trifle low from the retention of alkali by magnesia, the two errors counterbalancing. Pure hydrofluoric acid is, however, easily obtained, and the error due to magnesia might possibly be avoided by using carbonate of ammonium in the original extraction.

NOTE ON THE DETECTION OF CHLORINE, BROMINE, AND IODINE IN THE SAME MIXTURE.

By Joseph Torrey.

I read Mr. Kebler's note on the above subject in the October number of the JOURNAL with much interest. The problem is one of the most difficult in qualitative analysis. For an experienced chemist it is not so difficult, but the point is to find a method that can be used by students.

The object of this note is to describe some very slight modifications of Dr. Hart's method which in my experience have made it a little more convenient. The general procedure was given by Mr. Kebler and need not be repeated here. I have found no occasion to modify the details so far as the evolution successively of the chlorine, bromine, and iodine is concerned; but the bulb tube arrangement figured in the original description, and the

methods for detecting the halogens as they come off have been modified as follows:

Instead of the bulb apparatus originally described I use a small tube having one small bulb blown on it, the tube being bent slightly away from the perpendicular about half an inch above where it leaves the cork. Above the bulb there should be about half an inch of tube left. The flask containing the mixture to be analyzed is charged with ferric sulphate as usual and the iodine evolved; a small piece of starch paper is held in the steam as it emerges from the tube and any iodine speedily shows itself. When the iodine has all been expelled by boiling, as will be seen by the negative indication of the starch paper, a crystal of potassium permanganate is added and, on heating, the bromine is evolved. For detecting it I use iodized starch paper in the same way as starch paper was previously used and any bromine is easily detected. The boiling is continued until all bromine is gone, when the chlorine is detected as usual.

The only points where care is necessary in giving this process to students are the following:

1. Care must be taken that very small quantities of substances are used. The merest trace of any one of the halogens will be detected with certainty and large quantities only waste time and fill the laboratory with undesirable fumes.

2. The boiling must be continued till no trace of bromine can be detected before testing for chlorine. The boiling must be quite brisk or bromine will be mechanically held back.

For delicacy, rapidity, and certainty I have yet to find an equal of this process. With a reasonable amount of [illegible] character of the mixture is practically immaterial. In the original paper it appeared from the published experiments (or so I suppose I had a hand) that a large quantity of bromine masks the iodine test. I have not found the same effect to be [illegible] when the starch paper is used to detect the iodine.

During the last two years of the Summer School of Chemistry at Harvard University I have had many experiments made on mixtures of very varying proportions and have never yet met with any but favorable and satisfactory results.

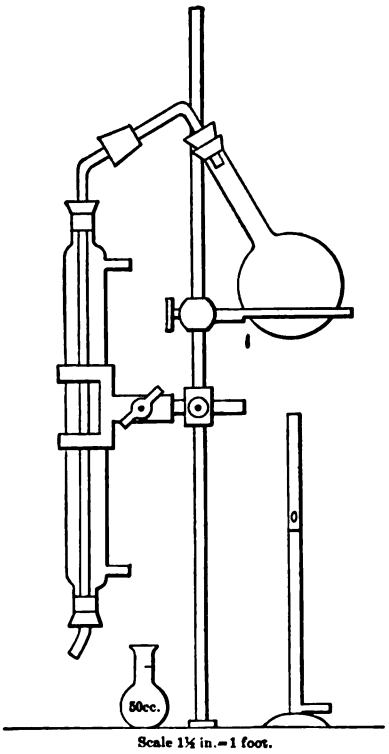
Last summer some work was done toward seeing whether the

process could not be turned to account quantitatively. The outlook was encouraging but the time was too short to accomplish enough to make it certain. I hope the work may be continued the coming summer.

APPARATUS FOR THE ESTIMATION OF FREE AND ALBUMINOID AMMONIA IN WATER ANALYSIS.

By Augustus H. Gill, Ph.D.

The article by Mr. Embry* upon this same subject, has induced me to describe the apparatus for these determinations in use in the laboratory for water analysis of the Massachusetts Institute of Technology, used by the State Board of Health.



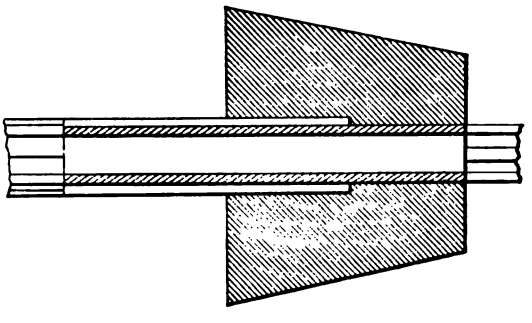
Scale 1½ in.=1 foot.

The arrangement will, I think, be evident from the accompanying sketch. The apparatus consists of a nearly spherical flask with square shoulders, of 850–900 cc. capacity, connected by a bent glass tube and "cork joint" with a vertical block tin condenser. The "cork joint" is here shown in section, and consists of a sound cork fitted at one end with the condenser, and at the other, with the glass tube, indicated by the cross hatching, which enters the former for about an inch and a half, thus avoiding all contact of steam with the cork, and making a tight and durable connection; the flask is closed with a superfine cork carrying the bent glass tube.

The condenser is the usual glass jacket, with the inside tube

* The Analyst, 17, 41.

of block tin, three ounces to the foot, one-quarter inch internal diameter, twenty-four inches long, and bent at the top for the "cork joint," and at the bottom for delivery into the fifty cc. graduated flasks.* The lamps used are ordinary Bunsen burners lengthened by inserting a piece of pipe between the base and the burner proper. The whole apparatus is supported by the ring and clamp upon a brass rod fixed into the distilling table. This



CORK JOINT
Full Size

table is eighteen feet long, two feet wide, and three feet high with two thirteen inch sinks near each end; upon it are arranged the two rows of brass rods five inches apart, with eighteen inches between each rod, thus affording space for fourteen sets of apparatus, and making the laboratory equipment capable of handling sixty to seventy samples per day. All the piping is underneath the table, the rubber tubing passing through it, one set of tubing being painted black to distinguish the rows; each condenser and lamp is provided with its own stopcock, or the whole can be turned off together.

For designating the number of the water analyzed, slips of ground glass are placed between the vertical rods.

The apparatus is distilled free from ammonia before each determination, and, as we have waters that show neither free nor albuminoid ammonia, it indicates that the working is satisfactory.

The condensation, even in the hottest weather, is absolutely perfect. Spiral condensers of glass and tin have been used, but

*Flasks are here used, as the Nessler tubes are inconvenient to manage; those in use hold 50 cc., are 8 inches long and ⅜ inch internal diameter, admitting of the reading of 0.000001 gm. of ammonia with absolute certainty.

were too fragile and cumbersome to admit of their continuance.

With this arrangement one person performs fourteen distillations simultaneously in about an hour, the work all being done from one side. The present form has been in use eighteen months, during which time about 5000 determinations have been made, which is sufficient proof of its practicability.

THE WEST AND WESTERN METHODS.

By Stuart Croasdale.

To the average eastern student the west appears as a kind of financial paradise where fortunes are rapidly accumulated and millionaires are the product of a few years, existence. While this is true to a certain extent, yet those who come with that idea in their minds will find the goddess as fickle here as elsewhere, and in the majority of cases the accumulation of wealth means hard work and close application to business.

Direct information and a few practical suggestions from a chemist's standpoint may be of value to those who contemplate coming west and it is such, as well as those who have written me personally, that the following pages are designed to answer.

Care has been taken to make the statements and methods embodied therein as reliable and complete as possible in order to give the student opportunity to familiarize himself with the field before entering it. It is not the purpose of the author to discourage immigration to the west but to produce a careful consideration of the matter, if possible, before a hasty step is taken.

The first thing to do of course is to secure a position. This is no easy matter for an eastern man, whether it be applied for while in the east or after coming west. Competition in this line is very sharp, for the supply of chemists and assayers exceeds the demand almost continually. The west is full of college graduates from all quarters of the globe. In the early days American students were almost ignored and Frieberg students were the ones sought for, but now the preference is given to the graduates of our own technical schools when an inexperienced man is employed.

Smelter superintendents and mine managers hesitate to employ men fresh from college, because, as a rule, they have had no training for western work. This is not so much the fault of the students as the fault of their instruction. Aside from a few technical schools the instruction in assaying is limited and not practical, and the instruction in chemistry is not broad enough, being confined for the most part to the iron industry. What many of our colleges need is a practical assayer to teach assaying and give a short course in technical methods of analysis after the student has been thoroughly drilled in the more delicate parts of chemical manipulation.

Outside of the large smelters a knowledge of assaying is absolutely necessary. This, it will be seen, brings the possible vacancies down to a few large works in Colorado located at Aspen, Denver, Leadville, and Pueblo; at Butte, Montana and in a few smelters on the plains. A good chemist having a position in a large plant may soon acquire sufficient knowledge in western work to take a position anywhere.

The work here differs to some extent from that usually required in the east, and with a few exceptions the methods used are much more rapid. Time is an important factor in all determinations. Volumetric methods are used whenever they are practicable. Separate samples are weighed out for nearly every determination so that as many as possible may be started at once. Tenth grams, one gram, or one half gram, as the case may require, are taken for analysis to avoid unnecessary calculation. Standard solutions are made so that one cc. = one per cent or [illegible] per cent. All these things, though small in themselves, mean a [illegible] saving of time when a large number of determinations are to be made.

The work varies with the metallurgical process in use. It consists of the assay and complete or partial analysis of the raw materials and the metallurgical products.

The raw materials consist of silicious, calcareous and [illegible] ores as well as pyrites and oxidized iron and manganese ores carrying gold, silver, lead and copper.

The determinations to be made include the assays for gold, silver, lead and copper and the wet determinations for lead, copper

silica, barium sulfate, lime, magnesia, iron, zinc, manganese, sulfur, arsenic, and antimony.

The metallurgical products consist of gold, silver, and lead bullion; sulfids, and lead carbonate precipitates from leaching works; copper and iron mattes, slag, and flue dust. The principal determinations to be made on these, besides the assays, are lead, copper, and sulfur on all but the last two. The analysis of the last two will be governed by the constituents in the furnace charge.

Besides the above there are numerous determinations to be made on the by-products that are constantly forming around leaching and amalgamation mills or a smelter; also analyses of salt, furnace gas, coal, crude sulfur, water, and occasionally qualitative tests and quantitative determinations on ore samples for platinum, tin, bismuth, and other unexpected metals. Western ores seem to contain nearly everything.

The methods used for the above determinations will be given in subsequent pages. The hours for work in a western laboratory are usually from 8 A. M. to 4 P. M. Samples brought in after 2 P. M. are not started until the next morning unless they are of special importance. Everything is done systematically; routine work usually occupies the morning and extra work is finished after that. When the work is done the chemist is free. Some companies require a full day, from 8 A. M. to 6 P. M., whether there be much or little to do.

Sunday work is universal, but in most places it is made as light as possible and can be finished by noon. In others it is the same as any other day.

In this, as well as in other parts of the country, the salaries are governed by two things,—the cost of living and the law of supply and demand. The ratio between the two is such that there is not much chance for the accumulation of wealth on an ordinary salary alone, whether that salary be earned in the east or in the west. Especially is this the case with a married man, for, besides having his family to support he cannot afford to leave one position to take another apparently more lucrative and run the risk of losing both. A single man can often take these chances, and even if he does not come out successfully he can

easily take care of himself until another position is open for him.

The regular salary in Aspen for a chemist and assayer is $1[illegible] a month. Assistants, and assayers who have learned the business from a position as "helper" in an assay office receive $1[illegible] a month. Chief chemists and assayers having complete charge of the assay office and laboratory receive $175 to $200 a month.

Board and lodging at a private house is $40 a month. Table board is $8 a week, although in a few places it may be had for $6. Furnished rooms are $10 to $15 a month.

Perhaps comparing these with eastern prices will show more than anything else.

EASTERN PENNSYLVANIA

12 months' salary at $60	$[illegible]
52 weeks' board and lodging at $5	[illegible]
Balance	$[illegible]

WESTERN COLORADO

12 months' salary at $150	$[illegible]
12 months' board and lodging at $40	[illegible]
Balance	$[illegible]

From each of the above statements must be deducted in about *the same ratio*, the cost of clothes, laundry and incidentals. Since these will vary with different persons the remainder of the calculation must be left for the reader. In all probability there will still be a balance in favor of the west.

The salaries in Leadville, Colorado, and in Butte, Montana, are practically the same as those just mentioned, while the cost of living is somewhat less. In Denver and Pueblo, Colorado, and farther east on the plains, the living expenses are $[illegible] to $[illegible] a month less and the salaries are correspondingly decreased. The above cities include the principal mining and smelting centers of this section of the country and the salaries are practically the same in smaller camps.

As before stated the essential feature in a chemist's knowledge for western work is that of assaying.

ASSAYING.

This subject cannot be more fully described than has been done in our best text books, but there are many little points, or tricks

perature, etc., that are of the highest importance, and yet the only way to learn them is to see the actual working of a furnace. The difference between an assay run in a "hot" furnace and one run in a "cold" furnace may be several ounces of silver to the ton, and yet in spite of the fact that the proper temperature is described in the text books how many students or inexperienced instructors will get it right?

The fluxing of ores will vary somewhat with the different mining camps. In most cases a plain scorification is used for all "control" work and specimen assays, while in some places it is customary to use the crucible assay, especially for the latter.

Perhaps the most troublesome ores in the United States to assay and analyze are the silver ores from Aspen. The gangue may be either limestone, dolomite, baryta, or silica, carrying lead, zinc, iron, and copper, wholly or partially combined as sulfid. Such ores not only necessitate a large number of wet determinations to make the proper ore mixtures, but even the scorification assay requires extra flux to get all the silver present.

Besides the assay of all the ore bought, there is considerable work to do with the furnace and mill products. Tailings, slags, and other low grade material are assayed in crucibles using one-half assay ton for each assay, while the salable products are made by scorification, the loss of silver in the slag and cupel being determined by an assay of the same or by running a check assay with the original.

The number of assays made in a day will vary, of course, as the samples are received. All things being favorable 125 to 150 assays are considered a day's work for one man.

THE CHEMICAL WORK.

Many of our western cities have omitted the gas epoch and start with electric light plants, so that a convenient form of fuel for the laboratory is not available even if the smelter or mill is fortunate enough to be located within reach of the city luxuries. Isolated gas plants are expensive to build and keep running in many parts of the west. Consequently a cook stove or a brick sand-bath heated with coal or wood, or an iron plate heated with oil stoves, serve for all evaporations. Alcohol lamps are used for

glass blowing, etc., and since the assay furnace usually precedes or at least accompanies the laboratory, all fusions and ignitions are made in the muffle. Fusions are made in platinum. Ignitions are made in porcelain crucibles, annealing cups, or scarifiers, and the residue is brushed out carefully and weighed by itself.

The methods used for the various determinations may be briefly described as follows:—

Silica and Barium Sulfate.—The ore is treated with strong hydrochloric acid or aqua regia or with strong nitric acid and a few drops of hydrochloric acid (if it is a sulfid), evaporated to dryness, taken up with strong hydrochloric acid, boiled, diluted, filtered, washed, first with hot water, then with a little hot ammonium acetate to remove any sulfate of lead that may be present, and finally with hot water, after which it is ignited and weighed. In the absence of barium sulfate this insoluble residue passes under the name of silica. If sulfate of barium is present the total weight is noted and the residue is fused with mixed carbonates in a platinum crucible. The fused mass is then digested with hot water which dissolves the alkaline silicates leaving the barium carbonate insoluble. This is filtered off, dissolved in hydrochloric acid, and the barium reprecipitated with sulfuric acid. The weight of the barium sulfate thus produced gives the percentage of that compound in the ore and that weight subtracted from the total weight previously obtained gives the percentage of the silica.

In slags (which are chilled by modern smelter practice) the silica is determined by treatment with hydrochloric acid as in the usual manner. The barium, which in this case was combined with the silica and has passed into solution, may be determined from the filtrate in the usual manner, or, more conveniently, by adding a little sulfuric acid to the sample which is to be used for the lime determination and throwing the barium down with the silica. The combined weight less the weight of the silica previously obtained will give the amount of barium sulfate. This is calculated to BaO.

Iron.—This is usually determined in the filtrate from the insoluble residue in ores or in the filtrate from silica in slags. It is

the permanganate and the bichromate methods are used without any modifications; the latter is more popular, owing to its greater rapidity.

Lime.—A separate sample of the ore is dissolved in hydrochloric acid, and a little potassium chlorate is added to oxidize the iron. The solution is then diluted, and the insoluble residue filtered off; ammonia is added to the filtrate until alkaline and then it is acidified with a strong solution of oxalic acid; ammonia is added a second time until alkaline, or until a brown color is produced, and the solution is again acidified with oxalic acid and heated to boiling. The oxalate of lime is then filtered off and washed until free from soluble oxalates and oxalic acid. The filter and precipitate are placed in a beaker containing hot dilute sulfuric acid (1 : 20) and the solution is at once titrated with standard potassium permanganate solution until a pink color is produced. One half the value in terms of iron = CaO. To insure good results the iron must be in a ferric state and the oxalate of lime must be thoroughly washed. With these precautions it is not difficult to get closely agreeing results. In the presence of much lead the iron and lead are precipitated with ammonia and the lime is precipitated from the filtrate with ammonium oxalate and titrated as described above.

In slags the original solution is evaporated to dryness to separate the silica and the residue is taken up with hydrochloric acid. (If barium is to be determined a few drops of sulfuric acid are added and the barium sulfate is filtered off and weighed with the silica.) The remainder of the analysis is the same as in that used for ores.

Some chemists prefer to ignite the oxalate of lime precipitaet in the muffle, but it requires a high heat and is not so satisfactory as the volumetric method.

Magnesia.—When required, the determination is made from the alkaline filtrate of a lime determination in the usual manner. Sometimes the process is shortened by weighing out a new sample and after dissolving in hydrochloric acid and oxidizing with chlorate of potash, the iron and lime are precipitated together by means of ammonia and ammonium oxalate and filtered off. The magnesia is then determined as phosphate in the filtrate.

Zinc.—Von Schulz and Low's method is recognized as the standard. This with other technical methods have been described in this JOURNAL* as well as in the *Engineering and Mining Journal*.†

Lead.—Lead in ore is always bought and sold on a fire assay but wet assays are frequently made. None of the wet methods however, seem to meet with universal approval, although a number have been proposed, each one claiming the essential features—accuracy, rapidity, and capacity of being used for all lead bearing products.

The method most commonly used is the bichromate method. The ore is treated with nitric acid and evaporated down with sulfuric to drive off the excess of nitric. The solution is then diluted and the insoluble residue containing sulfate of lead is filtered off and digested in hot ammonium acetate. This dissolves the sulfate of lead and after diluting it is titrated with a standard solution of potassium bichromate. The end reaction is determined by bringing a drop of the solution in contact with a drop of neutral silver nitrate solution on a porcelain plate, or better on filter paper. A red coloration shows excess of bichromate. Instead of converting the lead into sulfate the nitrate may be neutralized with ammonia or carbonate of ammonia excess of sodium acetate added, and the solution titrated as above described. (With low leads this method will be from one to three per cent higher than the fire assay, but with high leads it does not come up to the fire assay.) Another method consists in precipitating the lead as carbonate, dissolving in a measured quantity of normal nitric acid, adding neutral sulfate of soda solution and titrating the excess of acid by standard alkali solution. The lead solution should be free from other metals.

Among the other methods which may be mentioned are Von Schulz and Low's,‡ now used by the Penna Lead Co. in which the lead sulfate is dissolved in ammonium chloride and reprecipitated by aluminum foil as metallic lead and is weighed as such. Knight's§ method in which the lead is thrown down as an oxalate and titrated (like lime) with potassium permanganate

* [illegible]
† Engineering and Mining Journal [illegible] See also Low's paper in the [illegible]
§ This Journal [illegible]

Hawkins' bichromate method, in which the standard bichromate solution is added in excess. A measured quantity of standard ferrous ammonium sulfate is then added, and the excess of the latter is titrated back with bichromate, using potassium ferricyanid as an indicator; and Gallaher's method, in which the sulfate of lead is digested with strong sodium carbonate solution, and the precipitated carbonate, after washing, is dissolved in acetic acid and titrated with standard potassium ferrocyanid solution, using uranium acetate for an indicator as in zinc determinations. Still another method has been suggested but so far the details have not been worked out. It consists in dissolving the sulfate of lead in sodium thiosulfate and titrating with standard sodium carbonate solution, using methyl orange as an indicator. In presence of lime this method is not available.

Copper.—The cyanid method is used for ordinary work. The battery assay is used a great deal among the copper works in Butte, Montana, in connection with the cyanid method. The two may be made to check very closely by using the Swedish method in connection with the latter, *i. e.*, precipitate the copper with metallic zinc and then redissolve and titrate with potassium cyanid solution. In copper works where a number of matte samples are to be assayed for copper each day by the cyanid method a check sample is made up with a weighed amount of copper and iron that corresponds closely with the copper and iron in the matte, and this is titrated with the matte samples so the cyanid solution is restandardized each day.

Manganese.—Iles' method * is the one in general use. The ore or slag is treated in a casserole with concentrated hydrochloric acid until decomposed. A little nitric acid or chlorate of potash is added to oxidize the iron and the solution evaporated with sulfuric acid until all the hydrochloric acid is driven off. The solution is then diluted to 150 cc. and boiled. An emulsion of zinc oxid (ZnO and water) is added in large excess which precipitates the iron. This precipitate is filtered off and washed, the filtrate heated to boiling and titrated with standard permanganate solution. Instead of filtering off the precipitate of iron and excess of zinc oxid the solution may be made up to 500 cc.

* Engineering and Mining Journal, March 6, 1886.

and 100 cc. taken for analysis. The value of the permanganate solution in iron multiplied by 0.2946 = Mn.

Sulfur.—For ores and sulfids the "acid" method is preferable although fusion with potassium nitrate and sodium carbonate is used by some chemists; but this method gives high results owing to the formation of barium nitrate which is not readily soluble in water.

The ore or sulfid is mixed with a little chlorate of potash in a casserole, and after placing in cold water or snow strong nitric acid is added and the action is allowed to proceed slowly until solution and oxidation is complete. Instead of chlorate of potash potassium bromid is sometimes used. For ores containing but a small amount of sulfid, nitric acid alone is sufficient.

When action is complete the solution is evaporated to dryness to drive off the excess of nitric acid, the residue taken up with hydrochloric acid, the solution diluted, the insoluble residue filtered off, and the sulfur determined in the filtrate as usual by means of barium chlorid.

Iles' method for sulfur in slags is given as follows: One gram grams of finely pulverized slag is fused in a silver crucible with twenty-five grams of caustic potash for twenty minutes. The fused mass is allowed to cool, then dissolved in water and the oxids of iron, etc., are filtered off. Thirty cubic centimeters bromin water is added to the filtrate and the solution is acidified with hydrochloric acid, boiled to drive off the excess of bromin, filtered if necessary, and the sulfur is precipitated in the filtrate as usual by means of barium chlorid.

Arsenic.—Pearce's method as described in Sutton's Volumetric Analysis is considered as reliable as any. Instead of neutralizing the nitric acid solution with ammonia pure zinc oxid added in excess has been found to be equally as good and much more convenient.

Another method, by Messrs. E. N. and J. D. Hawkins is given as follows: Treat the sample with nitric acid, if decomposed evaporate nearly to dryness and then evaporate once with hydrochloric acid to destroy the nitric. Take up with hydrochloric, dilute, make strongly alkaline with caustic soda and precipitate with hydrogen sulfid. This precipitates the heavy metals as

ing the arsenic and antimony in solution. The latter seldom occurs and no attention is paid to it. Filter, wash, and decompose the filtrate with sulfuric acid. Allow to stand several hours and then filter off the precipitated sulfid of arsenic. Dissolve in hot nitric acid or hydrochloric acid and potassium chlorate and evaporate to small bulk. Dilute and add magnesium mixture and ammonia until strongly ammoniacal. Allow to stand twelve hours and filter off the magnesium ammonium arsenate. Wash with fifteen per cent. ammonia water, dissolve precipitate off the filter with dilute nitric acid (1 : 1) allowing the solution and washings to run into a platinum crucible. Evaporate to dryness, ignite and weigh as $Mg_2As_2O_7$. If the precipitate is ignited with the filter the arsenate is reduced and arsenic is volatilized.

If the substance is only partially decomposed treat the soluble part as described until the sulfid of arsenic is precipitated by sulfuric acid. Fuse the insoluble portion with six or eight times its weight of equal parts of sulfur and sodium carbonate at a low heat for twenty minutes to one-half an hour. Disintegrate in hot water and filter. Add sulfuric acid to the filtrate to precipitate the sulfid of arsenic, filter, combine this precipitate with the one previously obtained and proceed as before.

Antimony.—This determination is seldom required in ordinary work. The reader is referred to Crooke's *Select Methods* for a method of analysis.

The foregoing methods will cover all the analyses required in ordinary work. Special determinations must be obtained from the text books and periodicals as they are needed.

In conclusion the author would suggest to those who wish to come west and succeed in the chemical profession,

First, That they become thoroughly posted in inorganic chemistry, and also in *qualitative* as well as in quantitative analysis. While the methods just described will answer for routine work yet there are frequently cases in which the chemist must modify his work a little or make the determination in a different way as his judgment may dictate. A perfect knowledge of qualitative analysis will frequently help in quantitative determinations;

Second, That they come prepared to work hard and steadily

and be ready to take hold of anything in case they fail to secure a position at once, or in case they are suddenly thrown out of a position already obtained.

Lazy and incompetent men need not come. Employers have no use for them. With no one to recommend them they will find positions exceedingly hard to get, and at the same time they will find the west a poor place to live in under those circumstances. Competent men who are willing to work, and study with their work, will find the west a good field with excellent opportunities for advancement after a few years' experience.

ASPEN, COLORADO, DECEMBER, 1892.

THE VOLUMETRIC ESTIMATION OF ZINC.*

BY BERTRAND C. HIGMAN, PH.B., A.M.

The Colorado Scientific Society outlined a plan, some time ago, of endeavoring to establish a uniformity in the technical methods of analysis in the west. For its first effort, a committee of several chemists was appointed to investigate the methods for the determination of zinc in ores, and their report was presented to the Society in June, 1892.†

The ores submitted were from widely separated localities in Colorado; they were mixtures of galenite, pyrite, and sphalerite accompanied by greater or less percentages of manganese in the form of rhodochrosite, associated with a quartzose gangue.

To obtain a standard of comparison, the samples of ore submitted by the committee were analyzed by Mr. L. G. Eakins of the U. S. Geological Survey. The method followed by him was the conventional one—in short, as follows:

The ore was extracted with aqua regia, and the solution precipitated with hydrogen sulfid. In the filtrate from this precipitation the iron was separated by precipitating twice as basic acetate, and once with ammonia. In these filtrates (combined) and acidulated with acetic acid, the zinc was precipitated as sulfid, dissolved, precipitated as carbonate, and weighed as oxid.

Several chemists of metallurgical works in Colorado made analyses of the samples, and their methods and results are given in

* [illegible] Mines Quarterly, [illegible].

† This Journal, [illegible]

the report. They were, however, essentially like, or modifications of, the method of Messrs. von Schulz and Low, which received the approval of the committee. The operation is as follows:

"Prepare a solution of potassium ferrocyanid by dissolving forty-four grams of the pure salt in distilled water and diluting to one liter. Standardize as follows:

"Dissolve exactly 200 milligrams of pure oxid of zinc in a beaker in ten cc. of strong, pure hydrochloric acid. Now add seven grains of C. P. ammonium chlorid (the commercial article frequently contains a little copper), and about 100 cc. of boiling-hot water. Titrate the clear liquid with the ferrocyanid solution until a drop, when tested on a porcelain plate with a strong aqueous solution of uranium acetate, shows a brown tinge. About sixteen cc. of ferrocyanid will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing after each additional drop of ferrocyanid. As soon as a brown tinge is obtained, note the reading of the burette, and then wait a minute or two, and observe if one or more of the previous tests do not also develop a brown tinge. Usually, the end point will be found to have been passed by a test or two, and the proper correction must then be applied to the burette reading. Finally, make a further deduction from the burette reading of the amount of ferrocyanid necessary to produce a brown tinge under the same conditions when no zinc is present. This correction is about two drops, or 0.14 cc.

"200 mgms. of oxid of zinc contain 160.4 mgms. of zinc, and one cc. of the above standardized solution will equal about 0.01 grains of zinc, or about one per cent. when one gram of ore is taken for assay.

"Prepare the following solutions for the assay of ores:

"A saturated solution of potassium chlorate in nitric acid, made by shaking an excess of the crystals with a strong pure acid in a flask. Keep the solution in an open flask.

"A dilute solution of ammonium chlorid, containing about ten grams to the liter. For use, heat to boiling in a wash-bottle.

"A wash-bottle of hot water.

"Take exactly one gram of the ore, and treat with twenty-

five cc. of the above chlorate solution. Do not cover the casserole at first, but warm gently until any violent action is over and greenish vapors have ceased to come off. Then cover with a watch-glass and boil rapidly to complete dryness, but avoid overheating and baking. A drop of nitric acid adhering to the cover does no harm. Cool sufficiently, and add seven grams of ammonium chlorid, fifteen cc. strong ammonia water, and twenty-five cc. of hot water. Boil the covered mixture one minute and then, with a rubber-tipped glass rod see that all solid matter on the cover, sides, and bottom of the casserole is either dissolved or disintegrated. Filter into a beaker, and wash several times with the hot ammonium chlorid solution. A blue colored filtrate indicates the presence of copper. In that case, add twenty-five cc. of strong, pure hydrochloric acid and about forty grams of granulated test-lead. Stir the lead about in the beaker until the liquid has become perfectly colorless, and then a little longer to make sure that the copper is all precipitated. The solution, which should still be quite hot, is now ready for titration. In the absence of copper, the test-lead is omitted, and only the acid added. About one-third of the solution is now set aside and the main portion is titrated rapidly with the ferrocyanid until the end point is passed, using the uranium indicator as in the standardization. The greater part of the reserved portion is now added, and the titration continued with more caution until the end point is again passed. Then add the remainder of the reserved portion, and finish the titration carefully, ordinarily by additions of two drops of ferrocyanid at a time. Make corrections of the final reading of the burette precisely as in standardization.

"Gold, silver, lead, copper, iron, manganese and the rare earths constituents of ores do not interfere with the above scheme. Cadmium behaves like zinc; when known to be present it may be removed, together with the copper, by the proper treatment with hydrogen sulfid, and the titration for zinc may be made upon the proper acidified filtrate, without the removal of the excess of gas. There seems to be no simpler way of removing cadmium.

Notes on the above scheme.

"Acids destroy the delicacy of the uranium test, and so the

reason a strong aqueous solution of uranium acetate is used. By having the zinc solution only faintly acid, the production of the brown color of the end test becomes almost instantaneous, and no previous test will develop a color. Under these conditions, however, lead is apt to seriously interfere, and the excess of acid recommended above is found to be a necessity. When a strong solution of uranium acetate, not acidified, is used as an indicator, the error caused by the excess of acid in the zinc solution amounts to only two drops of ferrocyanid, which may be allowed for, and the brown tinge develops so rapidly that the end point is seldom passed by more than one test.

"When an ore contains but little copper, the granulated lead used frequently coheres in lumps that may hold zinc solution. These lumps are most easily broken up after a little of the ferrocyanid has been added. They appear to cause no appreciable error in the work. Of course, lead shot or thin sheet lead may be used, if preferred, and it may be cleaned with strong nitric acid and used repeatedly. It seems simpler and more satisfactory, however, to use the granulated lead and throw it away after use.

"As regards the use of nitric acid, it is found that the addition of one cc. of the strong acid to the boiling hot zinc solution during the standardization of the ferrocyanid, makes no appreciable difference."

The ores upon which these experiments were made were all from one section of country, and, in general, were ores adapted to lead smelting. It seemed advisable, therefore, to try the method upon ores from other places containing associated minerals different from the above. The Franklinite and Calamine ores are among the most important sources of zinc, and are very frequently dealt with in the metallurgy of that metal. Upon such ores most of the experiments were made.

The solutions were prepared as directed, with the exception that, for standardizing, metallic zinc was used instead of the oxid. The standardizing of the ferrocyanid solution presented no difficulty. If the solution is hot, the end-reaction shows promptly, but the amount of hydrochloric acid present must be regulated with some care, as an excess over that used at the time of standardizing will delay the end-reaction in titration to a sensible

degree. The practice adopted in making these experiments was to add a drop or two of methyl orange (though other indicators will answer equally well), bring the solution to the neutral point and then add a known excess of hydrochloric acid. The color produced by the indicator in no wise interferes with the end reaction during titration. By observing this simple precaution the solutions may always be of the same degree of acidity insuring perfect uniformity in the appearance of the end reaction.

At times, in dissolving the ore, all the potassium chlorate will not be decomposed, so that, when the solution is made acid with hydrochloric acid, just prior to titration, euchlorin will be set free. When using an indicator to determine the neutral point, its presence is manifested by its bleaching action upon the color. It is well, then, to add a few drops of a solution of an alkaline sulfite.

To test the process, a Calamine ore containing 60.50 per cent of zinc was carefully treated by the above-described method. There was obtained 65.14 per cent of zinc. The ore contained but little manganese, and the precipitate produced by the addition of the excess of ammonia consisted almost entirely of ferric hydrate. The residue and the precipitate was treated again with the chlorate mixture, the solution obtained evaporated to dryness, an excess of ammonia again added, and in the filtrate from this precipitation was found 1.62 per cent of zinc, making a total of 66.76 per cent. The experiment was repeated twice more in the same manner as at first. The three results were as follows:

	First Extraction	Second Extraction	Total
Per cent of zinc	65.14	1.62	[illegible]
" " "	65.37	1.41	[illegible]
" " "	65.36	1.41	[illegible]

The precipitated ferric hydrate held each time about one and one-half per cent. of zinc. This is a well-known phenomenon, but no mention of it seems to have been made by Messrs. [illegible] Schulz and Low in their description. This is undoubtedly because the ores worked by them contained so little iron that no appreciable difference was made by its presence.

In a fourth experiment on this ore an attempt was made to avoid the re-precipitation of the ferric hydrate by evaporating

the solution of the ore in the acid to dryness, and taking up with water instead of ammonia. Ferric nitrate seems to lose its nitric acid more readily than zinc nitrate, and by proceeding in this manner a filtered solution may be obtained containing only a small amount of iron. There was, however, enough present so that it was necessary to remove it with an excess of ammonia. There was found as a result 66.45 per cent. of zinc.

In order to determine the effect which the presence of manganese might have, a gram of this same ore was mixed with 0.2 gram of pyrolusite, and treated precisely as at first. There was found 66.76 per cent. of zinc, the manganese not changing the result. Thinking, perhaps, that the manganese dioxid would not be sufficiently decomposed in the strongly oxidizing solution used in decomposing the ore, another experiment was made upon the same ore with the same amount of pyrolusite present, but the mixture was first treated with hydrochloric acid to carry the dioxid of manganese into solution; nitric acid was added to expel the hydrochloric acid, and then the mixture was treated with the chlorate solution, and the analysis finished in the same manner as the previous ones. There was found 66.808 per cent. of zinc.

It may be safely concluded, then, that the presence of manganese does not interfere, and that it can be completely separated from zinc by oxidation to manganese dioxid in nitric acid solution.

A Franklinite ore containing 20.86 per cent. of zinc and considerable manganese was next tried. The first treatment of this ore gave as its result only 15.60 per cent. The residue re-treated with acid as before yielded 1.01 per cent., and the residue from this again treated gave up 0.50 per cent., making a total of 17.11 per cent. of zinc, or nearly four per cent. low. The experiment was repeated upon another portion of the same sample. There was found only about fifteen per cent. of zinc. The residue was re-treated as before and a little over one per cent. was found. The residue from this treatment was dissolved in hydrochloric acid, the iron separated as basic acetate, the filtrate made acid with acetic acid, hydrogen sulfid gas passed into it, and an abundant precipitate of zinc sulfid was obtained.

Evidently the solvent action of the nitric acid containing the potassium chlorate was not sufficient to completely decompose

the ore, so in the next experiment the following treatment was adopted.

The ore was first digested with aqua regia; nitric acid was then added, and the mixture evaporated until all the hydrochloric acid had been expelled, the whole evaporated nearly to dryness, the regular amount of the nitric acid solution of the potassium chlorate was added and the analysis finished as usual. As a result of this procedure, there was obtained 20.81 per cent of zinc.

A Franklinite, containing 23.53 per cent. of zinc, analyzed in duplicate in this manner, gave results respectively of 23.54 per cent. and 23.34 per cent. of zinc. Still another sample of the same kind of ore having 31.42 per cent. was found by the same treatment to contain 31.613 per cent.

Some of the ores tried, although very finely pulverized in an agate mortar, were yet not entirely soluble in aqua regia and it was necessary to fuse the residue in order to effect complete solution.

Copper was found to be easily separated in the manner described by the originators of the method, and the lead introduced and that which might otherwise be present, was found to have no injurious effect. In fact, at the end of a titration with the brown tint just faintly showing with the uranium acetate a large excess of lead acetate was added without changing at all the color of reaction.

The method of von Schulz and Low, as given by them, is an answer for ores easily decomposed and containing little or no [illegible] but to adapt the method to all ores of zinc or compounds containing it, cadmium alone excepted (which if present must be removed with hydrogen sulfid), certain modifications are necessary. Guided by the preceding experiments the following practice would seem most advisable.

Pure metallic zinc is more easily obtainable for standard [illegible] than the pure oxid. In standardizing and in actual analyses that the right degree of acidity be uniformly maintained the use of a color indicator in the solution is advised. It seems to be easier and simpler to work to the neutral point; this was [illegible] do it by means of test papers and the slight tint of color necessary to show the change to the eye does not impair the [illegible] reaction with the ferrocyanid.

The ore, if at all refractory, should be finely pulverized. A few moments spent in grinding will be more than compensated in the ease with which solution may be obtained.

Treat the finely divided ore with aqua regia until there is obtained complete decomposition, or until no further action is perceptible. If the ore has not been thoroughly decomposed, evaporate to dryness, dehydrate the silicic acid, take up with dilute hydrochloric acid, filter off the insoluble matter and fuse it with carbonate and nitrate of soda in a platinum crucible. Dissolve the fusion in hydrochloric acid and add the solution to the major portion. The dehydration of the silicic acid will consume some time, but if the ore is highly silicious, the gain of time in filtering the sandy precipitate of silica as contrasted with filtering the gelatinous silicic acid will be more than repaid. All the zinc in the ore will now be in solution as chlorid. Add nitric acid and boil until all the hydrochloric acid has been expelled; evaporate nearly to dryness, add the usual quantity of nitric acid saturated with potassium chlorate, and evaporate to dryness. Add the ammonium chlorid and ammonia, dilute with water, heat to boiling and filter, washing with a weak solution of ammonium chlorid made alkaline with ammonia. Transfer the precipitate from the paper, by means of a spatula and wash-bottle, to the vessel in which the ore was originally decomposed, evaporate off the water, and treat again with the chlorate mixture in the same manner as before, adding the solution obtained by treatment with ammonia to the original one. Acidify to the right degree with hydrochloric acid, heat nearly to boiling, and titrate with the standard ferrocyanid as described.

The details of the method as here worked out are more numerous than these given in the original article of von Schulz and Low, but it is apparent that to secure accuracy of results under varied conditions, they are necessary. It is still very much shorter than the conventional one, and carefully worked ought to give results nearly if not quite as accurate, and certainly the difficulties in manipulation are not so great.

In conclusion, I desire to thank Professor Elwyn Waller for his valuable suggestions in the preparation of this paper.

BRIMSTONE AND PYRITES AS RAW MATERIALS FOR THE MANUFACTURE OF SULFURIC ACID *

By Karl F. Stahl

The question has often been asked why the acid manufacturers in the United States have, until quite recently, been using brimstone, while in Europe pyrites has been used nearly exclusively for thirty years. This seeming backwardness is usually explained in a manner little complimentary to our home industry and even the report issued by the Geological Bureau of the United States for the year 1887 makes that mistake.

The author protests against this abuse and shows that if the variations in the price of brimstone, the history of our pyrites mines, the commercial situation in the period mentioned and the development of the industries using acid are considered an explanation can easily be found.

Whether brimstone or pyrites is preferable at a given place is not so easy to decide, and acid manufacturers hold views on this subject which differ widely from each other. Two articles have lately been published treating on this subject, one in this journal November, 1891, by Wm. H. Adams (Pyrites as a Material for the Manufacture of Sulfuric Acid). The second article appeared in the *Engineering and Mining Journal* of July [illegible] (The Comparative Value of Brimstone and Pyrites in the Manufacture of Sulfuric Acid) by J. H. Kelley.† The first very lengthy article contains many interesting statistical and historical notes about pyrites, but the theme itself is treated very one-sidedly in favor of pyrites. Mr. Kelley's article is short, but the statements it contains come much nearer the truth than those in the former paper.

For the burning of *brimstone* only simply constructed furnaces preferably made entirely of cast iron are necessary, and [illegible] no impurities get into the acid made from it. The ashes which are carried away mechanically with the gases, are deposited in the connecting pipes or Glover tower. The author considers the latter costly and sometimes troublesome apparatus unnecessary if brimstone is burned; with pyrites it is more useful [illegible] the gases and keeping the dust and part of the arsenic [illegible]

* Written in German and translated by the author from a [illegible] Association of Chemists at Buffalo, Sept. [illegible]

† See also article by J. H. Kelley in this journal, [illegible]

chambers; it also enables the manufacturer to keep the impure tower acid separate from the chamber acid.

For constructing a Glover tower usually so-called "chemical bricks" are used, but the author found that some kinds of paving bricks resist acid better, are smoother, and cost less than half the price of the former. Instead of quartz for filling a Glover tower, glass balls of about four inches diameter are recommended. Quartz can only be obtained in irregular lumps, which, on account of their sharp edges and corners, are difficult to handle, and exert a strong pressure against the sides of the tower, while hollow glass balls of about four inches diameter, which can be bought at a moderate price, are light, uniform in size, and cause an equal, and with each layer, varying distribution of the gases and acid.

Pyrites, as used in the manufacture of sulfuric acid, is not pure disulfid of iron, FeS_2, which contains 46.7 per cent. iron and 53.3 per cent. sulfur, but a mixture with other sulfids and gangue. Pyrites mined in the United States contains usually 39 per cent. to 42 per cent. sulfur, and besides iron, copper, zinc, traces of cadmium, and arsenic. Below are some analyses made by the author, expressed in percentages:

	1.	2.	3.	4.	5.	6.	7.
Moisture	....	....	2.9	....	....	1.3	0.8
Sulfur	45.1	37.6	37.1	50.2	43.7	40.6	42.4
Iron	....	40.6	41.5	....	....	37.3	35.4
Copper	3.1	5.2	0.6	....	....	1.0	1.4
Zinc	3.0	4.5	0.8	....	....	1.9	5.5
Cadmium	0.1	0.01	?	....	....	?	?
Insoluble	2.9	9.5	14.7	....	1.4	10.5	5.1
Arsenic	?	?	0.02	....	....	Trace.	Trace.

No. 1. February, 1882. Tallapoosa Mine, Ga.

No. 2. Average of several determinations made in 1884. Rogers Mine, Paulding Co. Mining Company, Dallas, Ga.

No. 3. Average of several determinations made in 1884. Sulfur Mines Company, of Virginia, Louisa Co., Va.

No. 4. November, 1882. Peru Zinc Company, La Salle, Ill.

No. 5. May, 1884. Dodgeville, Wis.

No. 6. November, 1891. Sulfur Mines Company, of Virginia, Louisa Co., Va.

No. 7. December, 1891. Davis Sulfur Ore Company, Davis, Franklin Co., Mass.

Each sample represented one or more car loads.

Pyrites is either sold as "lumps" or "fines," because each kind requires an entirely different furnace. The contsruction of furnaces for burning "lump" pyrites is well known. Furnaces for "fines" are either worked by hand or by machinery, but common to all is that the pyrites is spread out in thin layers on shelves arranged one above the other. Fresh pyrites is charged on top and gradually worked down. Schaffner's furnace is considered the best, although it is worked by hand, costing considerable labor, and the frequent opening of doors lets much gas escape. The Hammond-Spence furnace is worked by machinery, but it is difficult to keep it tight and the machinery causes much trouble.

A round furnace constructed by MacDougall Bros., of Liverpool, did not work satisfactorily, but it has been improved by A. C. Johnson, of Baltimore. Theoretically, this furnace is nearly perfect, and it works well as long as everything is in good order; labor is reduced to a minimum, the evolution of gas is regular, and as no doors are opened there is no loss of gas; but it must be constructed and tended with the utmost care, otherwise it will cause no end of trouble. The cinders weigh about three-fourths of the weight of the pyrites used, and contain, besides the oxids of metals present in the pyrites, undecomposed sulfids holding from one to five per cent. sulfur. American pyrites contains, usually, several per cent. of zinc, and as the zinc blende or the sulfate of zinc, which is formed, requires a higher temperature for decomposition than that reached in pyrites furnaces, the sulfur combined with zinc is not available. On an average, it can be assumed that the cinders contain four per cent. sulfur, which is equal to three per cent. sulfur in the pyrites. Copper is usually present in too small a quantity to make its extraction profitable, and its presence, together with the high percentage of silica, makes the cinder unsalable to iron works.

Besides the somewhat more complicated and more costly construction of furnaces, and the constant higher cost of labor in burning pyrites, there are other factors in favor of brimstone:

First, it requires less chamber space to produce the same amount of acid.

Second, lead chambers are said to last longer with brimstone than with pyrites.

Third, the acid produced is of different quality.

From the following equation it will readily be seen why pyrites requires more air than brimstone:

$$S + 2O = SO_2$$
$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2$$

The nitrogen, which enters with the oxygen, dilutes the furnace and chamber gases more in the second case than in the first, and causes them to be poorer in sulfurous acid. Theoretically, it would require 131 cubic feet of chamber space for pyrites against 100 cubic feet for brimstone. According to the author's experience, one-fourth more chamber space is sufficient to produce the same amount of acid, with the same consumption of niter.

It is very difficult to get exact figures on the second point, because the life of a set of chambers depends on so many circumstances, *i. e.*, quality of the lead, construction of the whole apparatus, temperature of the gases. whether the chambers are forced or not, and last but not least, on the care of management. It is claimed that arsenic in pyrites is very detrimental to lead, but this is not likely and the arsenic gets the blame, while it is the high temperature of the gases that does the harm. This, of course, could be avoided by proper construction, so as to cool the gases more before they enter the first chamber.

Concerning the third point, it has already been stated that from brimstone practically no impurities get into the acid. It is different with pyrites, especiallly when "fines" are used, which produce so much dust that the chamber acid resembles red wine; but for nearly all technical purposes this small amount of iron in the acid does no harm whatever. On concentrating, the oxid of iron dissolves and the red color disappears, without giving trouble in the lead pans or platinum stills, at least not if only commercial acid of 93 per cent. H_2SO_4 is made. A more harmful impurity is caused by the arsenic in the pyrites.

It may be remarked here, that pyrites from Massachusetts and Virginia always contains arsenic, claims of the mine owners to the contrary notwithstanding. The amount is small and it is difficult to detect it in the pyrites, but it can easily be determined in the acid made from these ores; it is however all precipitated in

the Glover tower and first chamber. Acid from the first chamber contains 0.005 per cent. arsenic; if all the chamber acid is mixed it contains about 0.002 per cent. arsenic, the acid being figured as 66° Bé. If pyrites richer in arsenic, like the Spanish is burned arsenic can be found in all the chambers in about the following proportion: First chamber, 0.16 per cent. arsenic, second chamber, 0.008 per cent. arsenic; third chamber, [illegible] per cent arsenic; fourth chamber, trace.

Fortunately the presence of arsenic does not interfere with many applications of sulfuric acid, for instance in the manufacture of phosphates and coal oil. These two industries use about eighty per cent. of all the sulfuric acid produced in the United States. But for the iron industry and for the production of all substances, which are used directly or indirectly as food or medicine, the sulfuric acid must be entirely free from arsenic.

Various processes are in use to purify acid from arsenic but in all of them the latter is precipitated as insoluble sulfid. Chamber acid to be purified has to be warmed and diluted to about 46° Bé. If large quantities of acid containing much arsenic have to be treated it is considered cheaper to use hydrogen sulfid made from iron sulfid and sulfuric acid. But for acids containing little arsenic the purification with a solution of barium sulfid is simpler and cheaper. Nothing harmful remains in the acid, most of the sulfate of barium and sulfid of arsenic settles rapidly and in a few hours the acid can be run through a suitable filter to get it perfectly clear.

It remains now to express the relative value of brimstone and pyrites in figures.

Mr. W. H. Adams, in the article mentioned above, figures the available sulfur in pyrites as equivalent or even better than brimstone. But anyone conversant with the subject can easily see that many of his figures are entirely wrong. For instance he calculates with brimstone a consumption of six per cent. nitre with pyrites only four and one-half per cent. nitre, assuming the same production of sulfuric acid in the same chamber space. He further calculates the work, cost of plant, wear and tear the same in both cases.

Mr. J. H. Kelley's calculations are more reliable but he [illegible]

in favor of brimstone. Although he assumes the chamber space necessary for pyrites to be one-third larger than for brimstone, he calculates 3.6 per cent. niter for brimstone and five per cent. for pyrites; he further calculates the wear and tear on a pyrites plant to be twice as much per ton of acid produced as on a brimstone plant.

The author makes the following calculation:

CHAMBER ACID FROM BRIMSTONE.

2½ tons brimstone (5600 lbs.), $21.00 per ton	$52.50
225 lbs. niter (= 4 per cent. of the brimstone), 2 cts. per lb.	4.50
220 lbs. sulfuric acid, 60° Bé., 40 cts. per 100 lbs.	.88
4 men at $1.50 (2 firemen for boilers included)	6.00
Wear and tear on buildings, furnace, chambers, etc., 40 cts. per ton chamber acid produced	5.40
Repairs on buildings, furnace, chambers, etc., 20 cts. per ton chamber acid produced	2.70
Fuel, light, etc.	2.00
Office expenses	5.00
Interest on capital invested	5.00
Product—13½ tons (2000 lbs. each) = 27000 lbs.	$83.98

1 ton chamber acid, 50° Bé., costs $6.22.

CHAMBER ACID FROM PYRITES.

5½ tons pyrites (= 12320 lbs.), 37 per cent. available sulfur, $6.00	$33.00
180 lbs. niter (= 4 per cent. of the available sulfur), 2 cts. per lb.	3.60
250 lbs. sulfuric acid, 60° Bé., 40 cts. per 100 lbs.	1.00
Breaking of the pyrites and removing the cinders	1.40
6 men at $1.50 (2 firemen for boilers included)	9.00
Wear and tear on buildings, furnaces, chambers, etc., 50 cts. per ton chamber acid produced	5.50
Repairs on buildings, furnaces, chambers, etc., 25 cts. per ton chamber acid produced	2.75
Fuel, light, etc.	2.00
Office expenses	5.00
Interest on capital invested	5.50
Product—11 tons (2000 lbs. each) = 22000 lbs., cost	$68.75

1 ton chamber acid, 50° Bé., costs $6.25.

It must not be forgotten that this is the cost of sulfuric acid 50° Bé. in the chambers, without the expenses incurred in con-

centrating, packing, handling, and losses in handling, etc., but these will be alike in both cases. If American pyrites are used, the cost of purifying the acid from arsenic is only about ten cents per ton.

We see that from pyrites containing forty per cent. sulfur, at $6.00 per ton, chamber acid can be made at the same cost, as with brimstone at $21.00. Forty per cent. pyrites yields about thirty-seven per cent. available sulfur; one ton of the latter therefore costs $\frac{6 \times 100}{37} = \$16.20$, and the difference between $16.20 and $21.00, that is $4.80, expresses the lesser value of a ton of available sulfur in pyrites compared with brimstone. From this the following table of values has been calculated:

Cost of 1 ton pyrites with 37% avail. sulfur.	Cost of 1 ton avail. sulfur.	Lesser value.	Corresponding value of 1 ton brimstone.
$5.00	$13.50	$4.80	$18.30
6.00	16.20	4.80	21.00
7.00	18.90	4.80	23.70
8.00	21.60	4.80	26.40

If, however, pyrites rich in arsenic is used, and all the acid has to be purified, the "lesser value" would have to be increased about $1.50, making it $6.30. Taking pyrites with forty-seven per cent. available sulfur at $8.00, one ton available sulfur would cost $17.00; add $6.30 and we get $23.30 as the corresponding value of brimstone.

Let us hope that the immense deposits of brimstone in our country can soon be made use of, and enable the acid maker to return to this ideal raw material.

TRINIDAD PITCH: ITS OCCURRENCE, ORIGIN, NATURE, AND COMMERCIAL APPLICATION FOR PAVING.*

By Clifford Richardson.

The island of Trinidad lies off the north coast of South America, between 10° and 11° of latitude and 61° and 62° of longitude. It is bounded on the north by the Caribbean Sea, on the east by the Atlantic, on the south by a narrow channel, into which flow the waters of the northern and most westerly mouths of the

* From a report to the Engineer Commissioner of Washington, D. C.

Orinoco, and on the west by the Gulf of Paria, the two latter bodies of water separating it from the mainland of Venezuela.

It is of an irregular rectangular shape, with promontories extending from its southwestern and northwestern corners which are several miles in length, between which and the mainland are the narrow straits known as the Dragons and Serpents mouths. These promontories form a large portion of the northern and southern boundaries of the shallow rectangular Gulf of Paria, whose outlets to the ocean are through the Dragons and Serpents mouths. The island has an average length of forty-eight miles and breadth of thirty-six, containing about 1,750 square miles and being about one-fifth the area of the State of Vermont. It is, as a whole, a flat country, with a high and striking mountain chain descending abruptly into the sea along its northern shore and with low central and southern ranges of less importance. Its coasts are naturally abrupt on the north, and consist of low bluffs on the south and are flat on the east and west. The only harbors are on the western coast.

The shape and structure of the long promontories which have been mentioned reveal the fact that Trinidad is, structurally, intimately connected with the main land. This is proved by the geology and fauna of the island, the latter corresponding closely to that of the mainland and the geological structure being a continuation of that of the continent.

Its climate is entirely tropical and somewhat different from that of the remaining Antilles in this respect.

Trinidad was discovered by Columbus on his third voyage in 1498 and taken possession of in the name of Spain, which colonized it about ninety years after. In 1797 it was taken by Great Britain, and has remained since then one of her most important West Indian colonies, and the second in size.

* * * * * * *

GEOLOGY OF THE ISLAND.

The island of Trinidad, while not directly connected with the chain of islands of volcanic origin known as the Windward or Caribbean Islands, is directly on the great line of volcanic disturbances running from these to the continent of South

America and its volcanic regions. Many of the Windward Islands are still possessed of active vents, so that Trinidad may be looked upon, with its thermal springs and pitch deposits as being situated at the lowest point between the mountainous volcanic chains of the West Indies and those of South America.

Its geology has been studied to any extent only by Wall and Sawkins, who in 1860 published under government auspices a "Report on the Geology of Trinidad, etc.," in which they give an elaborate account of the structural geology of the island and its pitch deposits. More than two-thirds of the surface is of tertiary or recent origin, including the entire southern portion where the pitch deposits are located. The formations consist of clay, loose sand, shales, limestones, calcareous sandstones, indurated clays, porcelainities of brilliant colors, with pitch deposits and lignite here and there. The beds have been considerably disturbed and have at times a large dip. In a series of loose sand, clays, and shales lies the Pitch Lake, with no calcareous formation near at hand.

Without lengthening this report with further references to the geological structure of the island, I would refer the reader desirous of examining the subject in greater detail to the original work of Wall and Sawkins, especially that portion denoted Appendix C.

THE PITCH DEPOSITS.

While there are deposits of pitch scattered all over the island, the only ones of commercial importance are those situated on La Brea Point, in the wards of La Brea and Guapo in the county of St. Patrick, on the western shore of the island. They are about twenty-eight miles in an air line from Port of Spain, the seat of government, the chief harbor and only port of entrance, and lie on the north shore of the southwestern peninsula, the point upon which they are situated being apparently preserved from destruction by the sea, which is elsewhere rapidly wearing away the coast, by the bituminous deposits which exist along the shore and even some distance from it, and which from their toughness resist the action of the waves better than the soft rocks of this region. The pitch deposits are found scattered over the point, but can be

divided conveniently into two classes, according to their source.

The main deposit is a body of pitch known as the Pitch Lake, situated at the highest part of the point.

Between this and the sea, and more especially toward La Brea, are other deposits, covered more or less and mixed with soil.

The pitch from these sources is classed as "lake pitch" and "land pitch."

THE PITCH LAKE.

By far the largest amount of pitch is found apparently in the Pitch Lake, a nearly circular area of 114.67 acres, 138 feet above sea level. From the lake the ground falls away on all sides, except, perhaps, a slight ridge to the east and southeast. In fact, it seems plain that this deposit lies in the crater of a large mud volcano which has filled up with pitch.

The crater is a flat, gently sloping mound, wooded over a large portion, open savanna elsewhere, and toward the north merely grassed over.

On the west its slopes toward the sea are gentle for some distance, but then more abrupt. On the north, toward La Brea Point, the reverse is the case, and a ravine runs, with a small stream, quite to the village, this slope being very scantily covered by a growth of coarse grass near the lake, becoming more bushy farther on, while the other slopes are well wooded, with magnificent palms near the lake, forming a beautiful band or border around it, within which is a grassy zone of about 100 to 200 feet or more in width.

As to the depth of the pitch deposits and of the crater many conjectures have been made, but none of them seem founded upon any basis of fact. At some little distance from the edges pits have been sunk as deep as twelve feet, in which pitch has welled up rapidly from the bottom, showing that there must be some feet more of the substance underneath. It is impossible, or has been impracticable, to sink deeper pits on account of the rapidity with which the pitch flows in all directions, and attempts to bore were equally unsuccessful in 1889.

In past times the pitch very probably continued to collect until it overflowed the rim of the crater in many directions, and thus

perhaps became the source of some of the land-pitch deposits now fonnd all the way from the lake to the sea.

At first sight of the Pitch Lake one sees a flat, dark expanse of pitch, dotted here and there with large clumps of shrubs and grasses, surrounded, except to the north, with a wall of palms.

On closer inspection it appears that the central portion of the surface is divided up by a network of pools, looking from a distance like shallow puddles of rain water. On walking over the lake, which is entirely possible, it will be seen that, while these pools are accumulations of rain water, they are deeper than would be expected, in many cases several feet, and, with their irregular shape, depend upon the fact that the pitch is not one homogeneous mass, but consists of spherical, polygonal, mushroom-like masses, which at the point where several come together form the spaces, which are filled with water.

These masses of pitch, slightly convex on the surface, are one of the most distinctive features of the lake surface. They range from thirty to two hundred feet in diameter, with a round, rolling edge, and coalesce more or less, depending upon the hardness of the pitch of which they are composed, there being a considerable difference in this respect between the edges and center of the lake. Owing to the softer nature in the center there are there fewer pools and shallower ones.

One of the most characteristic mushroom-like masses, situated near the central part of the lake, is an almost perfect circle of sixty-six feet in diameter. It has a convexity of one foot six and a half inches, and a very regular and typical formation, being neither too soft nor too hard to retain all the evidences of change of shape. It is the summit of one of the domes * * * * * * * * * * which reveals the wavy nature of the lake level caused by the dome-like masses and the depressed pools between them.

There have been several attempts made to explain the existence of these interstitial spaces without entire satisfaction, but it is plain to any observer that each large mass has a motion of its own by which the lower portions are brought up and roll out from the center to the edges.

This motion, with the aid of the water, preserves the circular

or polygonal shape of each mass and thus permits the continued existence of the star-shaped pools. The rolling motion is evidenced by the form of the edges and by sticks and other foreign substances which rise out of the pitch and assume various angles as the mass rolls toward the edge. The sticks often carry a cap of pitch which they have torn away from the surface, but they never have any adherent to the sides, nor will pitch adhere to wet substances. Gas bubbles or cavities which are found all through the lake pitch as they reach the surface are drawn out, with the movement of the mass toward the circumference, into fine lines, and the whole surface becomes covered with rings and wrinkles showing the concentric motion that is going on. This movement or rolling motion in the pitch is explained with greatest probability as due to alternate expansion and contraction of the viscous mass caused by changes of temperature between day and night, during the day the surface of the pitch reaching a temperature of 140° F., and at night falling to 80° or 90°, or lower. It may be also influenced by the continued evolution of gas in the mass.

The rain-fall of Trinidad is of tropical abundance, so that the joints are kept full at all seasons, and the water prevents the coalescing of the edges, although not that of change of shape, in the mass.

Notwithstanding the motion in the mass the pitch of nearly the entire lake is hard enough to walk over easily, and with the pick can be flaked out in semi-conchoidal masses of fifty to seventy pounds weight. A person standing for any length of time in one place would sink a slight distance, and a hole several feet deep will gradually fill up in a few days and disappear. This takes place by a pressure in all directions, upward as well as lateral, and is well illustrated in an experiment which was made at a point about three hundred feet from the edge of the lake.

A pit was sunk in the lake about three hundred yards from Station 25 on Monday, November 16, 11 A. M. Its changes in shape and rapid filling appear from the following measurements:

	Nov. 16, 11 A. M.	Nov. 16, 3 P. M.	Nov. [illegible] A. M.	Nov. [illegible] M.
Top:				
East to west	6 ft. 3 in.	6 ft.	5 ft. 7 in.	12 in.
North to south	5 ft. 3 in.	5 ft. 2 in.	5 ft.	
Bottom:				
East to west	4 ft.	3 ft. 6 in.	3 ft.	
North to south	4 ft.	3 ft. 5 in.	2 ft. 9 in.	
Depth	3 ft. to 3 ft. 3 in.	3 ft. to 2 ft. 8 in.	1 ft. 7 in.	[illegible] in.
Surface rises		3 in.	4 in.	

The changes show that the pressure was in every direction upward as well as lateral, and that the form the pit assumed was what we should expect as the resultant of forces acting in this manner in a viscous mass. In fact, Trinidad pitch whether in the lake or when taken elsewhere, illustrates most perfectly all the phenomena of glacial flow, and when stored in heaps soon becomes a solid mass, although brittle enough to be flaked with a pick at any time. It may be made a convenient means of illustrating many well-known geological facts.

Near the center of the lake there are in some of the spots patches of softer pitch, some of it so soft that a boy sinks to his knees in twenty seconds. It is not of different temperature from the harder pitch, in fact is a little cooler, owing to its surroundings, but it is of a brilliant, glossy black, like gas tar, and is filled with and continually emits gas. This gas near the edges of the mass is from time to time evolved with considerable violence and burns readily. It is largely hydrogen sulfid and carbon dioxid. The deposits of sulfur are seen about the rents, and the water has a strong mineral character and so mixed with the pitch that masses of the latter can be picked up and kneaded in the hands without its adhering to them.

At the soft spot the evolution of gas is so rapid as to be evident even to the ordinary observer, but it undoubtedly takes place to a smaller degree, at all times, all over the lake.

* * * * * The large conchoidal flakes of pitch picked out for shipping reveal the fact that all the lake pitch is honeycombed with gas cavities looking much like those in a Swiss cheese.

If the soft pitch is collected and in the laboratory allowed to stand in a closed vessel in a warm place it will continue to [illegible]

gas which can be collected; in fact, samples in sealed tin cans all exploded while coming from Trinidad, showing that a chemical reaction of considerable energy was going on. This reaction, without doubt, continues for a long time, as the pitch grows harder, and in conjunction with the surrounding physical conditions may somewhat influence the movement of the pitch in the mushroom-like masses.

Although the soft pitch is said by E. L. Joseph, in a history of Trindad published in 1837, to occupy a space of three and one half acres, it does not seem now to cover more than a few irregular joints amounting to a few hundred square yards.

A pole penetrates not more than six feet before striking hard pitch. The soft spot is, in fact, caused by the filling up of some of the old joints with soft pitch instead of water and it is chronicled that where an evolution of soft pitch is found beginning in a watery joint it arises to the surface in the shape of a mushroom.

In the neighborhood of the very soft pitch are found joints filled with semi-soft material and others with pitch of different degrees of hardness, so that it is very apparent that the soft stuff gradually changes and becomes like the remainder of the lake.

THE LEVEL OF THE LAKE.

In 1885, Mr. M. S. Manross described the Pitch Lake in the *American Journal of Science*. Of the pitch at the edge of the lake, where the road starts for La Brea, he says: "Here the pitch is bare or but slightly covered with grass. Its appearance is not that of a sudden simultaneous overflow in a single smooth stream, but that of a great number of streams, each but a few number of yards or rods in breadth." It is evident from this description that there must have been an actual overflow from the lake or crater at the time. To-day there is nothing of that sort to be seen, and the pitch outside the lake is well grassed over. This is undoubtedly due to the very large amount of pitch removed from the lake in the last twenty years, and is confirmed by the fact that on the east and west sides of the lake are well defined terraces of hard pitch, showing the old lake margins.

It appears that the level of the lake has fallen in the last few years about two feet, as evidenced by the terrace on the southern

margin, or, if this terrace is deceptive, as much as two-thirds of a foot, as shown by the terrace on the northern margin. I am inclined to believe that the northern terrace has been somewhat denuded and that the southern one is too high and that the lake has perhaps fallen in level a foot or a little more.

The surface of the lake appears from the plotted levels to be decidedly undulatory, especially in the center, which is at the same time higher than the southern side and quite as high as the northern, except in the immediate neighborhood of the soft spot. Had the levels been run from top to top of the mushroom-like masses instead of at regular intervals, which at times fell near the joints, probably some of the lower depressions would have been avoided.

THE LAND-PITCH DEPOSITS.

La Brea Point consists of a mass of hardened pitch deposits and reefs extending some distance into the gulf and along the shore in both directions. The deposits are found in greater or less abundance at all points between the shore and the lake, and directly along the line of the road, over an area estimated at a thousand acres or more. Two feet or more of soil cover the deposit at some distance from the lake, but near it the thickness diminishes and at places bare pitch is found.

On the point the pitch of the reefs is hard and resonant and has no cementitious value. The nearer the deposits are to the lake, however, the more viscous they become.

The incline from the lake to the gulf, a distance of three-quarters of a mile, is at first about one in twenty-five, gradually diminishing to the shore. Near the edge of the lake there is now a rank growth of grass, followed by shrubs and trees after passing the forks of the road. In the village, cultivated land is found, and large pits filled with stagnant water, from which pitch has been excavated. Except very near the lake, the pitch excavated from the land deposits is of a very different appearance from that taken from the lake, and it is also of several kinds.

The conchoidal masses removed from the lake, as I have said, contain large gas cavities, and in appearance and somewhat in

consistency resemble a black Swiss cheese. On this account the land pitch most nearly resembling this is known as "cheese pitch." It occurs in various degrees of porosity and life. In addition, land pitch is found in solid masses scarcely to be distinguished from refined asphalt, and this is known as "iron pitch." Pitch, known as "cokey pitch," from having been coked by the burning of the brush over its surface, and the chocolate and friable alteration products which have originated from atmospheric action and disintegration, are also recognized.

I am informed that in excavating for land pitch there is frequently found at that depth where the deposit seems to be about to vanish a dirty, black, sticky clay. In the same hole, therefore, it seems to be possible for all the different kinds of land pitch to be associated.

As can be seen in the * * * * specimens which have been collected, the land pitch has lost much of its viscosity, and does not become an easy yielding mass under the summer sun. It occurs, as described by Mr. Bowen, who was present at a time of more active excavation than I, "in all sorts of peculiar shapes, some as irregular columns, two or three feet thick and three to five feet high, others as long irregular mounds; some as beds with surface covered with irregular depressions and cavities, and all stiff and unyielding.

"Some of these pits make it appear as if earth, etc., constituted full three-quarters of the original mass before mining was done. In a few places in the village it was noticed that the half-hidden asphalt was on the surface of the ground, and that its edges presented the rolling character."

Mr. Bowen also says: "The origin of the asphalt and its erratic forms as seen in the villiage pits and of the bowlder-like masses along shore is obscure.

"It seems by their peculiar forms and their detached state as if this asphalt never came from the lake by overflow, but that it oozed up out of the earth through more or less small and somewhat scattered fissures, and that by long exposure to the elements and an ancient cessation from gas evolution it has long since come to differ greatly physically, and to a considerble degree chemically, from lake asphalt."

These views agree with those of Wall and Sawkins. We should have, then, land pitch derived from an overflow from the lake and land pitch from pockets where it has either originated or been pushed up along lines of least resistence from subterranean supplies. The presence of reefs along the shore and scattered masses from miles around, which could hardly be derived from the lake, and of springs of soft bitumen some distance south of the lake and also in the sea, points also to the fact that this view of the question is correct.

The deposits in the village, however, like the detached masses along shore, seem to be of considerably greater age than any others and of correspondingly little value for cementing purposes.

THE ASPHALT OF THE LAKE AND OF THE LAND DEPOSITS FORTY YEARS AGO.

I have quoted from a paper by N. S. Manross, published in the *American Journal of Science* in 1855, * * * * in which he gives a graphic description of the lake and the overflow from it, although the technical applications of pitch were then small. His observations are of value to-day as being unbiased and being made under circumstances which time has apparently largely modified. Some of his statements which are of present interest are as follows: He says, "In no part of the ascent from the shore to the lake does the pitch appear to be covered by more than one or two feet of soil, while in the most places it is entirely bare. * * * In places where the surface is not protected by vegetation, it becomes so far softened by the sun as to be still making progress downward. On nearing the lake the ascent becomes steeper, amounting to perhaps twenty-five feet in the last ten rods.

"Here the pitch is bare or slightly covered with grass. Its appearance is not that of a sudden simultaneous overflow in a single smooth stream, but that of a great number of streams, each but a few yards or rods in breadth. These independent streams have jostled one another strangely in their progress. Their surfaces are wrinkled and drawn out into all manner of contortions, and where the edges meet small ridges have been thrown up, and

the pitch broken into fragments not unlike the scoriæ of lava currents. These fragments of pitch were on fire in several places, having been kindled by a fire which ran through the 'bush' a few weeks before. The direction of the principal stream from the lake is to the north."

Referring to the pitch nearer the sea, he says: "In some places the bitumen is so mixed with earth as to lose some of its toughness as well as some shades of its pitchy hue."

From these observations it seems plain that there was practically an overflow as late as 1854 and a movement in the over flow pitch. There must have been, then, also much less growth on this overflow than at present, when it is scarcely possible to make it out even near the lake. The bush fires also account for the coke we have found. The reason of this gradual obliteration of the overflow stream and increased growth of herbage is due undoubtedly to the stoppage of the flow. Our investigations as to the relative level of the lake and crater sides * * * * * * prove that this has been caused by the removal of so much pitch in the times since 1854 that the level of the lake is so diminished as to prevent any continuance of the overflow. In the last twenty-five years nearly 300,000 tons of pitch have been taken from the lake, and as the influx is small the lake level has naturally been much reduced and the flow toward the village stopped. In consequence, herbage has grown up on the old surface and concealed the pitch more or less. The elements have then acted on it during a series of years and considerably altered its character. Even in Manross's time the older overflow appeared to him to have deteriorated.

Whether the entire supply of the point was originally from the lake can not be said, but in the light of the above observations of active movement in 1854 it appears probable that the flow may even in comparatively recent ages have extended a long distance toward the sea even while other masses of pitch may have broken out or originated in the soil at lower points independently of the lake, as suggested by Wall and Sawkins. In this case much of the land pitch must have been exposed for very long periods to natural conditions which would cause great deterioration and make it essentially inferior to the lake pitch.

Mannross's description of the lake structure and its movements is extremely graphic and well worth reading. Apparently there has been little change in appearances there since his time. In his paper he remarks that "various attempts have been made to apply the inexhaustible store of bitumen afforded by the lake to some useful purpose," apparently ignoring the land deposits as being of not much value. "Mixed with sand and pebbles it is much used for pavements and ground floors of houses at Port-of-Spain."

From the preceding description it is seen that there is a great deal of land pitch scattered over La Brea Point; that it is of various forms and qualities, and that while in the best excavations as much as 10,000 tons per acre may be obtained, other diggings do not afford in quantity or quality enough pitch to be remunerative. • • • • • • •

OTHER BITUMINOUS DEPOSITS IN THE ISLAND AND VICINITY

Some little distance south and west along the coast from the Point Boyer anchorage oil may be seen in spots upon the surface of the gulf, distinguished on a windy day by the comparative freedom from waves about it. This oil comes from submarine springs. On the shore just around the first small point [illegible] Point Boyer and about a mile west of the lake and on a slightly elevated bank, is quite a spring of liquid bitumen which in former times was worked with no commercial success. The oil [illegible] much sulfur and boils largely over [illegible] F. Another spring exists two miles south of the lake, and there are more at La Fortune on Iros bay, eight miles farther down the coast. In this neighborhood I believe considerable money has been spent [illegible] way of a tramway and plant for obtaining asphalt but the whole thing has now been abandoned.

Manross in his article in 1855 says: "From the point where the large spring of petroleum breaks out under the sea at least three miles of shore to the northward, consists mainly of strata of pitch from the lake. There are a few intervals of sandstone and clay where elevations have diverted the bituminous currents. But all the most prominent headlands are those which are extended by the indurated pitch. This material has flowed out [illegible]

a considerable, though as yet unknown, distance under the sea."

Either from a cessation of the flow or exuberance of tropical growth these appearances are not now visible, but this may well be, as Manross's description of the overflow toward La Brea is that of a scene very different from what one now sees.

This seaward overflow may be the cause of all the asphalt along the shore but it does not seem probable.

Much of this deposit must have, like the oil spring, arisen on the spot where it lies.

Bituminous deposits are also found on the Island at Montserrat on the southeast side of the hills, at Naparima, at Oropuche, at Quemada, and Moruga, and one of liquid pitch has been discovered at Mayaro in the last few months. At Guayaguayare, on the southern coast, there is a large lagoon covered with oil or soft pitch, and known as Lagoon Bouf from the fact that it boils up and makes quite a puffing noise at times. Submarine springs of bituminous nature are found at various points on the shore and even on the eastern or ocean side.

These bituminous deposits are of three kinds, the ordinary pitch, a pure glance, and oil. None of them are of any commercial value.

On the mainland there are several well-known pitch deposits and many salses or boiling springs. On the Pedronales River, one of the outlets of the Orinoco, an English company is now at work under a concession, and at Maturin, in the State of Bermudez, in Venezuela, a company is endeavoring to develop large deposits of bitumen.

COLLECTING AND SHIPPING OF PITCH.

There is no harbor at La Brea, and owing to the shoal water it is impossible for vessels which seek a cargo of pitch to lie nearer than from one-quarter to one-half a mile from shore. To them the pitch is brought in lighters holding some about ten tons and others smaller amounts. They are mostly provided with sails and are strongly built affairs, as at times, with a heavy northwest blow in the dry season, landing and unloading are rough work.

There are two points from which the lighters convey the pitch to

the vessels, La Brea Village and Point Boyer. * * * * * From La Brea both land and lake pitch are shipped; from Point Boyer only lake pitch. The county road runs from the lake to La Brea and furnishes the means for the collection and hauling of all the land pitch to the shore; the other road about a mile long, has been constructed for the special purpose of hauling lake pitch to Point Boyer, and is a private affair over land owned by the Trinidad Asphalt Company. At this point as much as [illegible] tons of pitch accumulate at a time and portions of it lie there as long as three months or more, running together into a solid mass. It is hauled there in two-wheeled dump carts with mules. There are about sixty carts in use at a time, hauling from six to ten loads a day between 4 or 5 A. M. and 2 or 3 P. M. Later than that it is too hot and the pitch is too soft to work. The estate has as many as eighty animals and others are hired by contract. They are furnished to the negroes with tools to work with and so much is paid for each load delivered.

At Point Boyer there is a shed where the pitch is weighed, a load generally being a short ton. It is then dumped in a heap directly upon the shore, or upon a rude pier, largely a rest and point of hardened pitch, but partially of artificial construction. Owing to the movement of the pitch and of the sandy bottom and the high northwest wind which blows at times, it seems difficult to maintain a suitable pier.

This heap of pitch runs very soon into a solid mass, and even the recent deliveries, must be picked to pieces again before loading into the lighters. This is done by negroes who load small baskets carried on the head or wheelbarrows with which they walk along a plank aboard the lighters and dump it in a pile in the middle. The quantity of pitch carried by the lighters is known, and from a tally of the number loaded on a vessel her cargo is calculated. Not until she is discharged in the [illegible] is the exact number of tons determined.

When two or more vessels are loading lighters may go to them both from Point Boyer and La Brea, there being a [illegible] lake pitch also at the latter place on the beach, which has been hauled there along the village road, and which is used as a [illegible] supply for the epure or refining works, which are situated [illegible]

From La Brea Point most of the pitch for the continent is shipped, largely in a refined condition. The crude pitch for this purpose comes from the edge of the lake, at its northern and northeastern edge, about where the road leaves the lake and near to the origin of the overflow. * * * * *

The pitch for Point Boyer comes from the northern, western, and southwestern borders of the lake, portions of convenient access to the two branches of the Point Boyer road.

All the lake pitch is taken from a belt 200 feet in width and about 200 feet from the border of the lake. Farther in upon the lake difficulties would arise preventing carts and mules from moving. The material is taken out in large conchoidal flakes, many weighing as much as seventy-five pounds. It has a rich, live look and is full of large gas cavities and shows some evidences of water mechanically entangled in the mass. In color, when fresh, it is a semi-lustrous bright black, with a brownish tinge, becoming more brown in drying. When refined, as in epure, it is a bright blue-black, even when powdered, and rapidly runs together and coalesces at summer temperatures.

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LAND PITCH.

Land pitch is obtained by excavation and separation from the earth with which it is mingled. It has been collected all the way from the lake to the Point and varies in quality vastly. Near the lake it has only a light covering of soil, a foot or less, produced by material collected upon it by wind and rain and by the rotting of the pitch itself to a friable condition. Near the point, in certain cases, the covering becomes many feet deep and the proportion of cheese pitch much smaller, but even at the same distance there is a great variation in localities, some spots furnishing thousands of tons to the acre and others not paying for excavation. Near the lake, naturally, cheese pitch is fouud fairly comparable with lake pitch, but even here some iron pitch and inferior stuff occurs, an indication that a change has already begun.

Consul Pierce remarks in his report:

"The cheese pitch of the land is firmer and stiffer (the more

so, it seems, the farther from the lake it is found) than the cheese pitch of the lake."

He considers—

"The difference was slight when two carts containing, one the lake, the other land pitch, were placed side by side. The lake pitch was somewhat brighter than the other and possibly of a more volatile appearance."

This from a person unacquainted with the technology of pitch is convincing of a remarkable difference, for if an entire novice can distinguish this in any way it must be actually very large.

TO BE CONTINUED.

NEW BOOKS.

Allen's Commercial Organic Analysis.*—This book bears evidence throughout of careful and conscientious work on the part of the editor. The original edition, which had 120 pages on the subjects here treated, is enlarged—not padded—to 584 pages in the present volume. The Amines and Ammonium bases are treated in 21 pages; The Hydrazines in 17 pages; the Bases from Tar in 88 pages; and the rest of the book is given to the Vegetable Alkaloids. The book is really a dictionary, for very full references to the literature of the subject are given under each heading, so that the study may readily be followed up. Such books are exceedingly valuable. The chemist—especially the analyst—is always busy, and anything which helps him to get needed information in the least time is sure to be appreciated.

The author defines the alkaloids, after Königs, as "those organic bases found in the plant kingdom which are pyridine derivatives".

The volume is beautifully printed on good paper and has two plates, after photographs, illustrating the tea leaf and the leaves of those plants commonly added as adulterants.

* Commercial Organic Analysis. By Alfred H. Allen. Second Edition, revised and Enlarged Volume III—Part II. Amines and Ammonium Bases, Hydrazines, Bases from Tar, Vegetable Alkaloids. Philadelphia: P. Blakiston, Son, and Company. 1892.

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